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CONTENTS.

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*THERMODYNAMIC PROPERTIES OF TWELVE LIQUIDS
BETWEEN 20° AND 80° AND UP TO 12000 KGM.
PER SQ. CM.*

By. P. W. Bridgman.

With seven Folders.

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Table of Contents.

I. INTRODUCTION.

THE experimental material of this paper consists of direct measurements of the volume of twelve liquids at different temperatures and pressures. The pressure range is from atmospheric pressure to 12000 kgm. per sq. cm., and the temperature range from 20° to 80°. The measurements were made at enough points to determine the volume at any pressure and temperature. These data are presented in the first part of the paper. The second part of the paper contains a discussion of a number of quantities of thermodynamic significance which have been computed from the data of the first part. The discussion is concerned only with the more important thermodynamic properties, namely the isothermal compressibility, thermal expansion, work of compression, heat of compression, change of internal energy, and the specific heats at constant pressure and constant volume.

Apparently the only other work of similar character at even comparatively high pressures is that of Amagat,[1] published in 1893. Amagat measured the volume of twelve liquids up to 3000 kgm. and between 0° and 40° or 50°. Beside the volume he tabulated the compressibility, dilatation, and pressure coefficient for some of the liquids, but the tabulation was by no means systematic or complete.

It is hoped that the material in this paper will afford the means for a renewed attack on the problem of the nature of the mechanism of a liquid. Theoretical speculation has been concerned hitherto chiefly with phenomena of liquids at low pressures, such as the latent heat of evaporization or the surface tension. At high pressures there are effects of another order, just as significantly descriptive of the internal mechanism, but as yet hardly touched by speculation. The data of this paper cover four times any previous pressure range, and should be sufficient to show the general nature of high pressure effects. Furthermore, the systematic presentation of different thermodynamic properties should afford different points of view for the attack.

The actual state of affairs at high pressures was found to be exceedingly complicated, contrary to what we might expect. We might suppose that the molecules would become so closely packed at high pressure as to allow less variety in their response to external changes, so that a liquid would approximate to a solid, in which compressibility and expansion change only slightly with pressure and temperature. A hypothesis of this character, backed up it is true by some experi-

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[1] Amagat, Ann. Chim. et Phys., **29**, 68–208 (1893).

mental evidence, has been made the basis of a recent empirical theory of liquids by Tammann,[2] who assumes that at high pressures variations in thermal expansion due to changes of temperature ought to become vanishingly small. Such, however, is by no means the case, but, on the contrary, at high pressures the thermal expansion varies with temperature in a more complicated way than at atmospheric pressure.

The irregularity of the effects at high pressures makes it evident that a complete theory of liquids must be very complicated. The first step, therefore, toward a theory would be to explain only the general features. With this in mind, the average of the various thermodynamic properties over the entire temperature range has been computed for each liquid. To facilitate comparison, the average of any one property, compressibility for example, is shown on the same diagram for all twelve liquids. One would expect to turn at first to these collected diagrams in seeking light on a theory of liquids.

In this paper no attempt has been made at the very considerable task of developing a quantitative theory to represent the data. The results suggest very strongly in some cases, however, that conceptions of the mechanism of a liquid which may be adequate at low pressures can no longer be adequate at high pressures. For instance, we shall probably have to modify our ideas of the mechanism accounting for pressure and temperature. Some discussion is given of modifications that may be necessary, and in several cases it is shown that the proposed modifications are competent to explain, at least qualitatively, the complicated effects found at high pressures.

A preceding paper on water[3] is very similar to the present one in the scope of its measurements and computations. The hope was expressed in the introduction to that paper that the projected study of twelve liquids (that is, this paper) would show what we might expect of a normal liquid, and that the results for water might then be compared with these results, and yield information about the abnormalities of water. This hope now appears to have been unfounded because no liquid is really normal at high pressures; all show individual peculiarities. It is true, nevertheless, that at high pressures these twelve liquids do become more nearly alike in a general way, and that water becomes increasingly like them. In many cases it will be found instructive, therefore, to compare the properties of water at high pressures with those of the liquids of this paper.

2 Tammann, Ann. Phys., **37**, 975–1013 (1912).
3 Bridgman, These Proceedings, **48**, 307–362 (1912).

The initial abnormalities of water have such a far-reaching effect, however, up to 6000 kgm., that it seemed desirable not to include water directly in the same diagrams with the other liquids.

The apparatus and the experimental method are in large measure the same as were used in the preceding work on water, and will not be described again in any detail. The methods of computation, however, are somewhat different, and are discussed at some length. It is impossible to give the original data because of lack of space. However, a few sample curves of the original data are given, and the average error of the compressibility and the expansion measurements is stated for each liquid.

The liquids used are with two exceptions the same as those used by Amagat. This choice of liquids has two advantages. In the first place, the present method does not give accurate results at the very lowest pressures, so that it is desirable to supplement the measurements with others at low pressures. For this purpose the values of Amagat for the change of volume between atmospheric pressure and 500 kgm. have been used. And in the second place, it was not desired to complicate this study, which is concerned with the liquid only, by the possibility of freezing under pressure. The freezing points of all the liquids used here are very low. It was hoped, therefore, that none of them would freeze under pressure at the temperatures of this investigation. The anticipation of no freezing was justified except in the case of acetone, which, however, froze at such high pressures that it was not necessary to discard it.

Comment should perhaps be made on the very extensive use of diagrams instead of tables. A table is capable of greater accuracy than a diagram, but a diagram has the advantage of presenting a large collection of results in a form immediately grasped. By the use of diagrams with fine rulings, the attempt has been made to combine the general grasp afforded by a diagram with the accuracy of a table. In most cases the numerical values may be read directly from the diagrams within the limits of experimental accuracy. The only exception is for the fundamental data, volume against pressure and temperature, for which tables have been given to four significant figures. The diagrams accompanying these tables are quite secondary in importance, giving merely a general survey of the trend of the results.

A brief indication of the plan of presentation may be helpful to the reader. The apparatus and the experimental method are first briefly described, indicating the points of departure from the previous

work on water (pages 7 to 18). Then the methods of computation are taken up in detail, describing in succession the method used for each one of the thermodynamic properties (pages 18 to 37). A somewhat detailed analysis of the data for each liquid is next given, including any special features of the experiment for that liquid, the experimental error, and the source and probable accuracy of data by other observers which have been used in the computations (pages 37 to 74). Here are included the fundamental data for each liquid, that is, the tables and diagrams of volume against pressure and temperature. The various thermodynamic properties are then discussed, with comments on the peculiarities of the individual liquids, and on the general features common to them all (pages 74 to 104). The diagrams for this general discussion are given on folders at the end of the paper, all the diagrams for any one property being collected on one sheet. It is hoped that this arrangement will produce less confusion in the text, and at the same time, permit a more ready general survey of the facts. Finally, there is given on pages 104 to 113, a discussion of the bearing of the results on previous theories, and of the possible effects on our ideas of what the actual mechanism of a liquid may be.

II. Experimental Method.

The method is essentially similar to that used in the preceding work on water. As in the earlier work, so here, the liquid under investigation is placed in a cylinder closed by a piston which moves absolutely without leak. The pressure on the liquid may be varied by changing the position of the piston, and the temperature may be varied by altering the temperature of the surrounding bath. The volume is found directly by measuring the position of the piston in the cylinder. The fundamental data to be obtained with the apparatus are the values of the volume as a function of pressure and temperature at a sufficient number of points to allow the calculation of the volume at any temperature and pressure within the range.

In actual use the simple procedure suggested above is complicated by the necessity of introducing the instrument for measuring the pressure into the same cylinder with the liquid under investigation. The pressure in these experiments was measured with a coil of manganin wire, the changes in the resistance of which give the pressure by a previous calibration.[4] Although this manganin gauge is compact

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[4] Bridgman, These Proceedings, **47**, 319–438 (1911).

and simple, its use introduces complications, because it must come in contact only with a liquid that is an insulator. The water of the preceding paper and nearly all the twelve liquids of this are not insulators. Some auxiliary liquid must be used therefore, to transmit pressure to the manganin coil. Kerosene has shown itself perfectly adapted to the purpose, and has been used in all this work. In the former work on water, the kerosene and water could be allowed to come directly in contact with each other, but in this investigation, nearly all the liquids are more or less miscible with kerosene, so that means had to be provided to prevent the liquid under investigation from coming into contact with the kerosene. This necessitated slight changes in the design of the apparatus, and the use of still a third liquid, mercury, to keep the liquid and the kerosene from direct contact. The modified receptacle for holding the liquid is shown in Figure 1. The liquid is enclosed in a steel bulb A, the stem of which dips into the cup B containing mercury. The cup B is bored out at the lower end so as to protect the manganin pressure gauge, which is shown at C. The bulb, cup, and gauge together occupy the lower part of the pressure cylinder. In order to obtain as large a quantity as possible of the liquid to experiment on the diameter of the bulb etc. was made larger than that of the moving piston ($\frac{11}{16}$ inch against $\frac{1}{2}$ inch). To allow this the cylinder had to be bored out at the lower end to the larger diameter. In other respects the cylinder is similar to that used for water, in fact it is the same cylinder, the only change being the enlargement of the lower part to meet the new requirements.

FIGURE. 1. The compressibility bulb with attachments. *A* is the bulb containing the liquid under investigation. *B* the mercury cup, and *C* the insulating plug and the manganin coil with which pressure is measured.

The final form of receptacle shown in Figure 1 was arrived at only after a considerable number of failures. Early attempts to use glass cylinders, which from the point of view of purity would be more desirable, had to be abandoned because of the invariable fracture of the glass. This is doubtless because kerosene under pressure becomes

so viscous as not to transmit small changes of pressure hydrostatically immediately after changes in the position of the piston. The enormously increased viscosity both of the kerosene and of the liquid under investigation within the bulb afforded the only satisfactory explanation of many of the capricious misfortunes of the preliminary work. For instance, in the early work the bulb was closed at the upper end by a cap put on with soft solder. Several times after the application of pressure this soft solder was found eaten away by the mercury. The only apparent way in which this could happen would be by the liquid (ethyl alcohol in the preliminary investigations) becoming so viscous as to crack as the volume decreases with rising pressure, thus allowing the mercury to rise through the cracks from below. Another very troublesome effect in the preliminary work was the frequent short circuiting of the manganin coil by small drops of mercury. These were probably forced out of the cup by the viscous motion of the kerosene during changing pressure. The difficulty was avoided by making the lower part of the mercury cup in the form of a protecting cap for the manganin coil, and by enlarging the channels of communication between the cup and the bulb from the kerosene to the mercury. It was found also that it was necessary to give the bulb fairly thick walls. Otherwise, when pressure is relieved, the bulb expands under the viscous motion of the fluid inside and tightly fills the cylinder. Furthermore, the bulb must not fit the cylinder too closely, for otherwise the pressure is not transmitted rapidly enough to the interior of the bulb, which may thereby become collapsed at the upper end. Still again, the upper end of the bulb must be provided with radial grooves to give access from the lower to the upper part of the cylinder, or else when pressure is released, the entire bulb rises with the viscous kerosene against the ledge on the cylinder, acting effectively as a valve which permits only comparatively slow release of pressure, with the result that eventually, when pressure is released, the top is blown off the bulb and forced into the smaller bore of the cylinder above.

It must be a matter of experiment to find the dimensions for any particular piece of apparatus which will avoid all these difficulties. Complete success was attained, however; the last twenty out of a total of twenty-four runs being completed without accident of any kind.

Although the method outlined above is exceedingly simple, yet there are evidently a number of corrections for the distortion of the steel

containing vessel and for the auxiliary liquid.   These corrections have been discussed in great detail in the preceding paper on water.   The corrections to be used in this paper are exactly similar to the former ones, with the exception of the correction for the effect of the mercury. It will be recalled that two sets of measurements are necessary to obtain all the data needed in making the corrections; the first is with the steel bulb filled with the liquid under investigation, and the second with the liquid and bulb replaced by a cylinder of Bessemer steel. The quantities of kerosene are approximately the same in the two sets of measurements.   If the quantity of mercury used in the two sets were exactly the same, it would not be necessary to apply any correction for it, but since it was not easy to use exactly the same quantity, a correction for the difference had to be applied.   This correction was exceedingly small, being merely the change with pressure and temperature of the small difference, and could be obtained with sufficient accuracy for this purpose from measurements already made on mercury up to 12000 kgm. at 0° and 20°.[4] The variation of compressibility and dilatation with temperature is so small at high pressures that it is perfectly safe to extrapolate to 80°.   The quantities of mercury in the two determinations seldom differed by as much as 0.3 gm., in which case the correction can be entirely neglected.

The altered design of the containing vessel made necessary a modification of the procedure in filling the cylinder ready for a run.   The bulb was filled by boiling the liquid into it at reduced pressure at room temperature.   During the filling the liquid came into contact with a gum stopper for a few seconds.   The bulb was then disconnected from the air pump, and gently warmed by holding it in the hands, thus forcing a slight quantity of liquid out of the stem.   After the bulb had come to the temperature of the hand, the outside was carefully wiped dry, and the stem immediately inverted into the cup of mercury.   In this way the complete exclusion of all air bubbles was ensured.   After the bulb had once more come to the temperature of the room, the combined weight of the filled bulb, mercury, and steel cup was found.   The weight of the liquid in the bulb can then be found immediately by subtracting the known weight of the mercury, cup, and bulb.   The quantity of the liquid used in the majority of the experiments was about 12 c. c.   The mercury cup with the bulb still in place was now slipped over the manganin resistance coil,

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[4] Bridgman, These Proceedings, **47**, 319–438 (1911).

and the coil, mercury cup, and the liquid under investigation were inserted together into the cylinder.   This naturally had to be done from below, and for this purpose the cylinder was held vertical during this operation in a special vise, projecting at right angles from the wall. The packing and the retaining screw were also inserted while the cylinder was in this position.   The cylinder was now filled with a weighed quantity of kerosene through the open upper end.   This filling with kerosene was accomplished in two operations; first, half of the kerosene was poured in, and all air extracted from the lower part of the cylinder by gently exhausting it, and then the remainder of the kerosene was poured in.   The moveable plug was then inserted, with special care not to spill any kerosene, and finally the cylinder, kept always upright, was put in position in the lower part of the press.   After a run the bulb was cleaned for the next run by heating it nearly to redness.   That the cleaning was thorough was shown by the constancy of weight of the bulb, which seldom varied more than one milligram from experiment to experiment.

The essential idea of the experimental method remains the same as in the work on water, but there are slight modifications.   The purpose is to obtain by direct measurements the change of volume with pressure over the entire pressure range at some one constant temperature, and then by another independent set of measurements to obtain the change of volume with temperature over the entire temperature range at a sufficient number of pressures to completely cover the field. This method has a distinct advantage over that employed by Amagat, for example.   Amagat obtained the volume as a function of pressure and temperature by measuring the change of volume with pressure isothermally at a number of temperatures.   This has the disadvantage that the thermal dilatation can be found only by taking the difference of compressibility determinations at different temperatures.   Obviously this makes it necessary to measure the compressibility with a much greater degree of accuracy than the desired final accuracy of the dilatation, and this is a difficult matter to accomplish.   But the present method gives both compressibility and dilatation with the accuracy to be expected of direct measurements.

The procedure in measuring the change of volume with pressure at constant temperature was the same as in the work on water.   The temperature chosen for this determination was 40°, because it is the same as was used for water.   Reference is made to the former paper for the details of manipulation.   In order to cover completely the pressure range, it was necessary to make the readings in two series,

one at lower pressures up to 2000 kgm., and the second between 2000 kgm. and the maximum, 12000 kgm. A similar method was found necessary in the previous work on water. The reason for this is that at high pressures the moveable piston takes a permanent set, and moves with extreme friction against the sides of the cylinder. The result is that if the pressure has once been pushed to the maximum the piston will not return far enough to reach the low pressures again. The lowest pressure that it was possible to reach after the maximum varied somewhat, but was usually in the neighborhood of 1000 kgm. In order completely to cover the field, therefore, two sets of experiments were necessary, one for the high and the other for the low pressures. To make the results comparable, the low pressure measurements were carried some distance into the high pressure domain, the upper limit of the low pressure measurements being about 2000 kgm.

The chief variation from the method of the earlier work is in finding the thermal expansion. The method of the earlier work involved two steps. The first was to change the temperature at constant volume. This change of temperature, if it were an increase, produced as a secondary effect a rise of pressure. The second step was to lower the pressure to the original value preparatory to the next change of temperature. The withdrawal of the piston necessary to effect this lowering of pressure was always attended by slight irregularities; apparently the piston does not begin its regular march until after some slight motion has taken place. So that although perfect regularity was found in the larger motions of the piston of the compressibility determinations, yet the initial irregularity was sufficient to be disturbing with the smaller motions accompanying the temperature changes. The difficulty was avoided by keeping the piston constant in position during a series of temperature changes, and allowing the pressure to vary accordingly. The variation of pressure for a change of temperature of 60°, from 20° to 80°, was about 1000 kgm. at the highest pressures, and proportionally less at the lower pressures. Temperature measurements were made at six values of the average pressure with the apparatus set up for the higher pressures, above 2000 kgm., and at two mean pressures with the apparatus set up for the lower pressures, below 2000 kgm. Readings were made at 20° intervals, as in the work on water. At 2000 kgm., for example, the temperature was raised from 20° to 40° and the increase of pressure noted, then to 60° and the increase of pressure noted again, and finally from 60° to 80° and once again the increase of pressure noted.

The pressure was then increased at 80° to the next higher value, about 3500 kgm., and the corresponding set of measurements made at 20° intervals, this time with decreasing temperature. The other four sets of readings were made in a similar way. The highest pressure reached, on the last reading at 80°, was about 12500 kgm. From here the temperature was decreased, so that the final reading at 20° was made at a pressure of about 11500 kgm. Here is an incidental advantage of the modified method of making the expansion measurements, because mercury solidifies at 20° at less than 12000 kgm., so that if the former method had been used a smaller value of the mean maximum pressure would have been necessary for the last reading at 20°. Of course the modified method necessitates a slight change in the method of making the computations, which will be described later.

All the measurements on each of the liquids were repeated to ensure greater accuracy. The measurements were made in two series; all twelve liquids were first measured, and, except for the preliminary experiments, no repetitions made until at least one set of readings had been made for each liquid. This has the advantage of separating the measurements on any one liquid by a considerable interval of time, and thereby eliminating any possible effect of temporary variations in the apparatus. During the first extended series of readings the two sets of readings for each liquid at high and low pressures were made with two separate fillings of the apparatus. At the lower pressures the viscosity effects do not play any part, so that it was not necessary to leave so large a space between the bulb and the walls of the cylinder as was necessary for the higher pressures. In this way a larger bulb could be used at the lower than at the higher pressures, so that somewhat greater sensitiveness could be obtained at the lower pressures because of the greater quantity of liquid. But this made it necessary to take the apparatus apart after the set of readings at low pressures, and replace the larger bulb by the smaller one for the run at high pressures. This made considerable trouble, which did not seem adequately compensated by the somewhat greater accuracy, so that in the repetition of the experiment the readings at the high and low pressures were all made with the same filling of the apparatus. The readings at low pressures were made before the readings at high pressures, and so before the piston had been upset.

The final detailed procedure was as follows. The readings at low pressures were made first. It is not necessary to describe them in detail as they were similar to the readings at the higher pressures, the

only difference being that no seasoning precautions were taken. At
high pressures the thermostat was first adjusted to 40°, and then the
cylinder seasoned over the entire pressure range by advancing the pres-
sure to the maximum and releasing it three times. The details of the
seasoning process are described in the former paper. The compressi-
bility measurements at 40° were then made. Readings were taken
both at increasing and decreasing pressures, so as to correct for hy-
steresis. The range of these measurements was from 2000 to 12000
kgm., returning after the complete set of readings to the initial pres-
sure of 2000 kgm. Next, the cylinder was seasoned for the thermal
expansion readings by advancing the pressure to 11500 kgm. raising
the temperature to 80° at constant volume, releasing the pressure
to 2000 kgm. at 80°, and finally reducing the temperature to 20°. The
thermal expansion measurements were then made by the method
already described.

In the later form of procedure, in which the effects at high and low
pressures were measured with the same set-up, all the measurements
at the low pressures and the isothermal compressibility at 40° were
made on the same day; on the next day the thermal dilation at six
mean pressures was measured, and the apparatus taken down and set
up again with a new liquid ready for another run on the next day.

By the use of large reservoirs of hot water and by nearly emptying
the thermostat at every change of temperature, it was possible to
make the readings with changing temperature fairly rapidly, the
elapsed time between readings at successive temperatures being
about fifteen minutes. A much longer time than this would have
been necessary to secure temperature equilibrium throughout the
mass of the cylinder if a special device had not been adopted. This
consisted in running the temperature past the final value, and then
returning to it. Thus, let us suppose that the temperature was to
be changed from 20° to 40°. Water was drawn from the thermostat
and enough hot water poured in to raise the temperature to 45°, and
not until the lapse of several minutes, the exact time to be determined
by experiment, was the temperature reduced to 40° and the regulator
set at this final value. After some practise it was possible to reach
temperature equilibrium in little more time than was necessary for
the manipulations of drawing water and putting in fresh. Readings
were never made, however, until at least three minutes had elapsed
without change of pressure.

The actual experiments, after the preliminary work, occupied four
months, from February through May, 1912. Many of the early

measurements are due to the assistance of Mr. S. L. Gokhale.   During the entire time there was no change in the internal diameter of the cylinder of so much as 0.0001 inch.   To ensure further that there was no progressive change in the cylinder during the measurements, the comparison measurements with the liquid replaced by Bessemer steel were made at five intervals during this time.   The maximum divergence of any of these readings from the mean was only 0.5%, better perhaps than would at first be expected from the method.

The original data are so numerous that it seemed undesirable to give them here in full.   Every point recorded involves six readings, two of pressure and four of piston displacement.   On the average each liquid involved 140 points, 75 for compressibility and 65 for thermal expansion.   This makes a grand total of 12500 readings in the original data.   It was thought to be sufficient to give a few sample curves of complete data, and to state for each liquid the average departure from the mean of the two series of compressibility and dilation measurements.   The average departure from the mean of the two series of compressibility measurements for the twelve liquids was 0.15% of the maximum, and the departure from the mean of the thermal expansion measurements was 2%.   The changes of volume due to changes of pressure are much greater than those due to temperature, so that the compressibility measurements determine the final accuracy of the volume.

In regard to the purity of the liquids, it was not thought necessary to take special precautions, because the properties studied here are not much influenced by the presence of impurities.   The compressibility, for example, of a mixture of two liquids of small concentrations of the one in the other is an additive function of the compressibility of the two components.   An example of this fact occurred in the preliminary work on ether.   The first measurements were made with the ether enclosed in a glass bulb.   This bulb broke on the application of pressure because of the great viscosity of the kerosene.   The compressibility measurements of this preliminary run were measurements, therefore, on a mixture of ether and kerosene.   In spite of the fact that this ether was very much contaminated the result showed that the compressibility of this mixture was only different by 4% from what it was when the measurements were made on the same quantities of ether and kerosene prevented from mixing.

The liquids used were obtained from Eimer and Amend.   They were either the purest manufactured by them, or else Kahlbaum's purest.   It was to be expected therefore, that only slight impurities

were present, and that the errors due to them are beyond the limits of observational error.

Nine months after the completion of the experiments, the remaining samples were subjected to a rough analysis by determining the boiling points. If the liquid is pure, the boiling point should remain constant until the liquid is completely boiled away. The amount by which the boiling point changes during evaporation can be expected to give at least some clue as to the amount of impurity present. [A substance is considered good enough for most *chemical* purposes if it all boils within 1°.] Of course this analysis does not give the nature of the impurity present, nor does it give the impurity at the time the experiment was performed. During the nine months the liquids were left tightly corked, but there can be no question that some deterioration had gone on in this time, so that the liquids were all actually better than is indicated by the analyses. The deterioration with time is much greater for some liquids than for others.

The fractionations were performed by Mr. R. H. Patch at the Chemical Laboratory of Harvard University. The results of his examination are given below. It should be noticed that the temperature readings have not been corrected, so that all they can show is the constancy of the boiling point, not its absolute value.

Methyl Alcohol (Kahlbaum).

93% boils between 64.5° and 65° C.

7% " " 65° and 65.8° C.

Free from ethyl alcohol and acetone, the most likely impurities, and was neutral to litmus. Excellent sample. (It would seem that the impurity was probably water, most of which had probably been absorbed while standing, as the stopper was not perfectly tight).

Ethyl Alcohol (Kahlbaum).

3.8% boils between 77.3° and 77.8° C.

96.2% " " 77.8° and 78.0° C.

The sample showed some suspended inorganic matter, probably iron from the container. (The sample had been standing for the nine months tightly corked with a cork stopper in the tin vessel in which it came from Kahlbaum). With this exception, and admitting the presence of a small quantity of water the sample was a good one.

Propyl Alcohol (Kahlbaum).

4.% boils below 96.° C.

96.% boils between 96.0° and 96.8° C.

A good sample.

Isobutyl Alcohol (Eimer and Amend).

    7% boils below 105.8° C.

    17% boils between 105.8° and 107° C.

    76%   "   "   107.0° and 107.2° C.

    Thus 93% boils within 1.4°, a good sample.

Amyl Alcohol (*Kahlbaum, Free from Pyridin*).

    3% boils below 128.9° C.

    89.5% boils between 128.9° and 129.9° C.

    7.5 boils between 129.9° and 130.0° C.

    Sample free from foreign organic matter and neutral to litmus. An excellent example.

Ethyl Ether (*Kahlbaum, "Sp. gr. 0.720"*).

    The whole sample boiled between 34.5° and 35.0° C.

    Neutral to litmus, free from aldehydes, and sulphur compounds.

    Contained some water, and without doubt some alcohol.

Acetone (*Eimer and Amend. Marked "Pure"*).

    70.6% boils between 56° and 57° C.

    19.4% boils between 57° and 58° C.

    10% boils between 58° and 59° C.

    The sample left a dark brown residue in the distillation flask, probably aldehydic in nature. Free from water, and neutral to litmus. A fair sample. (The brown color developed on standing; at the time the experiment was performed, the liquid was perfectly colorless.)

Carbon Bisulphide (*From the store room of the Chemical Laboratory*).

    5% boils between 45.8° and 46.° C.

    95 boils at 46.0° C.

    The sample was free from hydrogen sulphide, sulphuric and sulphurous acids, but contains some foreign organic sulphur compounds and left a yellowish residue. The latter always results upon allowing the liquid to stand, especially upon exposure to light. (Here again the color had developed upon standing during the nine months. At the time of the experiment the liquid was perfectly colorless.)

Phosphorus Trichloride (*Eimer and Amend*).

    True boiling point is 78.3° C.

    Sample showed no constant boiling point.

    6.5° boiled below 77° C.

    11.2% boiled between 77° and 79° C.

    17.9% boiled between 79° and 80° C.

15.9% boiled between 80° and 81° C.

17.9% boiled between 81° and 87° C.

31.4% boiled between 87° and 102° C.

Chief impurity probably phosphorus oxychloride formed by combination of the trichloride with the moisture in the air, also some pentachloride is almost always unavoidably present, due to excess chlorine.

Ethyl Bromide (Eimer and Amend).

The whole sample boiled from 38.0° to 38.4° C. and with the exception of not over 2% at 38.4° exactly. Neutral to litmus, an excellent sample.

Analyses could not be made of the ethyl chloride and the ethyl iodide, because these samples were completely used up in the experiment. Both of these were obtained in sealed glass bulbs from Kahlbaum, were used immediately after opening, and were both colorless when used.

These analyses show that probably none of the liquids contained enough impurity to have any perceptible effect, except the phosphorus trichloride, and to a less degree the acetone. The phosphorus trichloride was very noticeably simpler in its behavior at high pressures than the other liquids; probably due to the fact that it is a mixture of different substances, and so can not be expected to show the well marked behavior of a single pure substance.

A few measurements were made on one liquid which are not tabulated here. These were measurements on chloroform, which was found to freeze at fairly low pressures, about 6800 kgm. at 40°, and 10000 kgm. at 80°. Further investigation of this liquid has been postponed until a systematic investigation of freezing curves can be taken up.

III. Methods of Computation.

The methods of computation were slightly different from those used in the work on water, in part because of the somewhat different experimental method. They are, in consequence, here described in detail. As in the computations for water, the first step was to prepare a table giving the volume at regular intervals of pressure and temperature. From this table the other thermodynamic quantities were then computed.

The Table of Volumes. In preparing the table of volumes, the first computation was of the volume as a function of pressure at 40°. The first step was to plot the piston displacement against the displacement

of the slider of the bridge wire on which the resistance of the manganin coil was measured.   Because of hysteresis effects it was necessary to make two sets of readings, one with increasing and the other with decreasing pressure.   Care was taken that any two corresponding readings should be at as nearly as possible the same pressure, so that it should be allowable to take the average of two corresponding displacements as the best value of the displacement at the average of the two corresponding pressures.   The next step was to draw a smooth curve through the average points, and from the curve to tabulate the displacement at regular intervals of pressures (5 cm. on the bridge wire, or about 1100 kgm.).   The second series of measurements on the same liquid was then treated in the same way.   These two series of measurements differed somewhat as to the quantities of materials used, that is, the liquid under investigation, the kerosene, the mercury, and the steel.   But the amounts were so nearly the same that it was permissible to take the average displacement of the two series as the displacement that would have been found for the mean between the quantities of material used in the two series.   In only a few cases did the amounts of material in the two series differ so much that it was not permissible to do this.   In these cases the displacement for the mean quantity had to be determined in a way which need not be described in detail.   The average of the displacements obtained in this way were now corrected for the effect of the kerosene, the mercury, the steel, and the distortion of the steel containing vessel. In applying the corrections, the mean of the five auxiliary experiments in which the liquid was replaced by Bessemer steel was used.   The correction was applied in essentially the same way as for water. The corrected result gave the motion of the piston due to the compression of only the liquid under investigation.   This, with the known cross section of the piston and the weight of the liquid, determined the change of volume at any pressure of 1 gm. of the liquid.   Finally, by using the values for the density at 0° deduced from the recent Tables of Kaye and Laby, the results were reduced to the change of volume in c. c. of a quantity of liquid which at 0° C. and atmospheric pressure occupies 1 c. c.   This is the unit quantity which is here adopted throughout, and seems to have been most usually used in work of this kind.   In particular it is the unit quantity of Amagat.

The computation just described applies only to the measurements at the higher pressures.   The results are tabulated as changes of volume from 2000 kgm. as the zero of pressure.   If the pressure during the high pressure measurements went lower than this, as it usually did,

the corresponding changes of volume were taken as negative. To obtain the volume at lower pressures, the measurements at the lower pressures were reduced in much the same way as has been described for the higher pressures. One difference is that the measurements at the lower pressures were at 20° instead of 40°, because several of the liquids boil at less than 40° at atmospheric pressure. It was not possible to reach entirely to the zero of pressure with the low-pressure measurements, because of the slight friction of the piston even when the pressure had not been pushed so high as to permanently upset the piston. It was not possible to get much nearer to zero than 100 or 200 kgm. after the pressure had once been pushed to 2000 kgm. In order to come still closer to zero, several measurements were made during the very first application of pressure, before the cylinder has been seasoned for hysteresis. During these first readings the pressure was increased to about 1000 kgm. and then seasoned for hysteresis as before. As a result the second set of readings between 200 and 2000 kgm. made after this seasoning process did not make close connection with the first set. The discrepancy was due in part to hysteresis, but also in part to better adaptation of the packing to all the crevices in the steel washers. The direction of the two curves was usually the same, however, within the limits of error. This allowed an extrapolation to zero by combining the results of the first set of readings with those of the second. In this way the change of the unit volume from atmospheric pressure up to 2000 kgm. was determined. It must be remembered, however, that the readings at the very lowest pressures are almost certainly in error, because the instrument is not designed for low pressures. But with increasing pressure the readings become more and more trustworthy, until above 500 kgm. they seem to merit entire confidence, if we can judge from self consistency. To get the total change of volume from atmospheric pressure it is desirable, therefore, to supplement these readings with others made with apparatus especially designed for low pressures. Such measurements are afforded by the data of Amagat, and in some cases by others.

At the time that the computations of this paper were made, the data of Amagat were the best that we had for the compressibility at low pressures. Between the time of computing these results and writing this account, however, there has appeared a paper by Richards,[5] in which the compressibility up to 500 kgm. of several of the liquids

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5 Richards, Jour. Amer. Chem. Soc., **34**, 971–993 (1912).

used here is determined. It is unfortunate that these values did not appear in time for use in the present computations. They are quoted, however, so as to afford a comparison with the results of Amagat, which are here used as the standard for low pressures. It makes no difference with the essential conclusions of the paper, however, which set of data is accepted as most probably correct. The only effect would be to change the initial values of some of the thermodynamic properties; their magnitudes at high pressures will not be altered.

The precise steps in combining into a final result the changes of volume computed from the two sets of readings at high and low pressures were as follows. From the high pressure readings, the changes of volume at 40° (ΔV, cm.^{3}/cm.^{3}) were plotted against the displacement of the slider of the resistance bridge, the zero of pressure being at 10 cm. displacement. The scale of the diagram was large; 2 cm. for 0.1 inch piston displacement, and 55 cm. slider displacement for the maximum pressure. From the low pressure readings ΔV in cm.^{3}/cm.^{3} was found at 20°, and was plotted against slider displacement, the zero being at 5 cm. A smooth curve was drawn through these points. From this curve, knowing the constants of the manganin coil, ΔV was found at 500, 1000, 1500, and 2000 kgm. and 500, 1000, 1500, and 2000 atmos. ΔV in terms of atmos. was now corrected so as to be reckoned from 1000 atmos. as zero. The values of Amagat for ΔV at 20° were next computed with 1000 atmos. as the zero. These two sets of data were compared, and the new values for the lowest interval adjusted so as to be in agreement with Amagat between 1 and 500 kgm. It will be noticed that this preliminary comparison with Amagat does not enter the final result; it was an orienting comparison for obtaining some idea of the accuracy at low pressures. Using Amagat's value for the lower interval, the changes of volume at pressures corresponding to 2.5, 5.0, 7.5, and 10.0 cm. were next determined, reckoned from zero pressure. These values were now corrected to 40° with the data obtained for the thermal dilatation and were recomputed with 10 cm. as the zero of pressure. The changes of volume at 40° obtained from both the low and high pressure sets of measurements were now plotted together on one diagram, and a smooth curve drawn through the points. From this curve the changes of volume with the kilogram as the unit of pressure were read off at 500 kgm. intervals, starting from an origin at 500 kgm. The changes of volume so found were now smoothed to give regular differences. The smoothing was performed in a manner somewhat different from

the corresponding operation for water, and in a manner which has the advantage of preserving the irregularities which are shown by experiment actually to exist, but which would have been effaced if the attempt were made to give smooth second differences, as was done for water. In performing this smoothing, the fact was used that the change of volume of nearly all the liquids can be represented by a curve of nearly the same shape. Ethyl chloride is an exception, and a special computation had to be applied to it. As a first approximation the change of volume of the other eleven liquids was found to be reproducible by a formula of the type;

$$\Delta V = \alpha \left(\frac{p - 500}{1000} \right)^{.8} + \beta \left(\frac{p - 500}{1000} \right)^{.6} + \gamma \left(\frac{p - 500}{1000} \right)^{.4} + \delta \left(\frac{p - 500}{1000} \right)^{.2}.$$

In order to apply this formula to any one liquid it is necessary simply to multiply all four constants by the same factor. The meaning of this is that to this degree of approximation the chief difference of the liquids with regard to changes of volume is in respect to the absolute, not the relative magnitudes of the change. The constants of the above formula were computed, therefore, so as to apply to the average of the eleven liquids. This was done by finding the average change of volume for the eleven liquids at 1500, 3000, 7000, and 12000 kgm. and determining the four constants of the formula so that the curve should pass through these four points. It will be noticed that in this formula the zero of pressure is at 500 kgm., so that it applies directly to the changes of volume as found above. The formula was now applied to the eleven liquids in succession by multiplying the four constants by the appropriate multiplier for each liquid. The multiplier was so determined that the formula should give the observed change of volume at 7000 kgm. The changes of volume were now calculated with this formula at intervals of 500 kgm. up to 5000 kgm., and beyond 5000 kgm. at intervals of 1000 kgm., and compared with the observed values. The differences between the observed and the computed values were plotted on a large scale and a smooth curve drawn through the points. The values obtained from these smooth curves and the formula were combined to give the final values for the volume at 40°. The advantage of the method is that the final results lie on perfectly smooth curves, and that the curves show the various slight irregularities which correspond to the experimental facts but which would be smoothed out if the second differences were made uniform. The values for ethyl chloride were

treated in the same way, except that it was necessary to start from a slightly different formula, to be given on page 67.

It would have been possible to dispense with this finer adjustment by means of a difference curve with very little change in the final result, because the changes of volume obtained from the original

TABLE I.

METHYL ALCOHOL.

DIFFERENCE BETWEEN VOLUME OBTAINED FROM ORIGINAL SMOOTH CURVE AND FINAL COMPUTED VALUE.

Pressure. kgm. cm.^{2}	Difference.	Pressure. kgm. cm.^{2}	Difference.
500	.0000	5000	−3
1000	− .0000	6000	+2
1500	−1	7000	−3
2000	0	8000	−1
2500	−1	9000	0
3000	+1	10000	0
3500	−2	11000	−1
4000	+1	12000	0
4500	0		

smooth curves were almost the same as given by the final computation. Table I shows for one liquid (methyl alcohol, chosen at random) the very slight changes made by this readjustment.

The values obtained by this computation start from 500 kgm. as the zero. The change of volume between atmospheric pressure and 500 kgm. has been taken directly from the results of Amagat in those cases where his data are sufficient. In some cases where Amagat does not give the data, it has been necessary to use the more inaccurate values of the present method. In the detailed presentation of data for each liquid, the values taken from Amagat are given. If it should happen at any future time that more probable values than these of

Amagat are found for the changes of volume at low pressures (which indeed is already the case for those liquids measured by Richards), then the results given here may be corrected by adding a constant to the volumes throughout the tables, except of course at atmospheric pressure. The addition of such a constant to the volumes will not alter the behavior of any of the thermodynamic properties at high pressures; it can at most affect those which involve integrations by a very small constant corrective term.
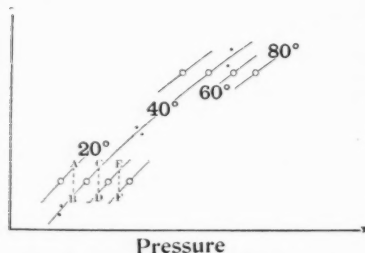

Pressure

FIGURE 2. Shows a portion of the diagram for determining the compressibility and thermal expansion from the piston displacements. The piston displacements are plotted against pressure. The heavy points are the readings with increasing and decreasing pressure at 40° for the isothermal compressibility. The discrepancy between these points is due to hysteresis. The open circles show the readings at constant volume with changing temperature. The dotted lines, *AB* for example, show the piston displacement which would have been found if the temperature had been changed at constant pressure.

That it was possible to represent the approximate behavior of these twelve liquids by similar formulas is itself a somewhat surprising and significant fact. It seems to suggest that at extremely high pressures all liquids become alike. The greatest differences between different liquids are at the low pressures. The use of a separate formula in the case of ethyl chloride, which might appear to be an exception, was necessitated in fact only by its abnormal compressibility at low pressures.

It was necessary to compute the thermal dilatation also by a method slightly different from that used for water, because only one piston displacement was read at each temperature instead of two. The piston displacements were plotted against pressure on the same diagram as the isothermal compressibility at 40°. (See Figure 2.) Through each of the points a curve was drawn of the same general slope as the curve of pressure and volume at 40°. The slight changes necessary in the slope of this curve at different temperatures could be made graphically with sufficient accuracy. The difference of the piston displacement for every interval of 20° at the mean of the two pressures involved was now read from these curves. Thus in Figure 2, the line AB represents the piston displacement at constant pressure

corresponding to a rise of temperature from 20° to 40°, CD from 40° to 60°, and EF from 60° to 80°. These displacements correspond to slightly different values of the mean pressure. The piston displacements at constant pressure obtained from a diagram like Figure 2 were then plotted against pressure on another diagram, the points for the two independent series of measurements on the same liquid being plotted on the same sheet. The quantities of liquid used in the two series were usually so nearly the same that the mean of the piston displacements could be assumed without error to be the piston displacement of the mean quantity of liquid. The mean of the two independent series of readings was found graphically from the diagram by drawing a smooth curve through the two sets of points. From this value of the piston displacement, after corrections had been applied for the kerosene, mercury, and steel, the change of volume per unit quantity for intervals of 20° was computed in a way analogous to the similar computations for the compressibility. Here again the values for the low pressures are most likely to be in error. The change of volume at 20° intervals at atmospheric pressure was taken directly from the tables of Landolt and Börnstein. Finally, the experimental points and the points at atmospheric pressure were plotted together on a single diagram, smooth curves drawn through them, and from these curves the changes of volume for intervals of 20° were obtained which were used in the construction of the tables of volume.

In plotting as above on a single diagram ΔV for 20° intervals, two independent series of measurements, namely those of this paper and those on which the formulas of Landolt and Börnstein are based were therefore brought together. The two sets of data should of course, if consistent, lie on a smooth curve, so that the amount of discrepancy might be expected to afford an indication of the order of accuracy at low pressures. The change in the dilatation is, however, so rapid at the low pressures that it was possible in nearly every instance to make smooth connection between the two sets of points, without departing from either of them. Furthermore, it would be possible in most cases to make just as smooth connection if somewhat different values were used at atmospheric pressure. Slight discrepancies between the smooth curves and the individual points do not therefore, give a reliable indication of the accuracy.

The thermal dilatation is probably not so accurate as are the changes of volume with pressure, because the dilatation is much smaller. The dilatation can be measured with no greater accuracy than the changes of pressure accompanying the changes of temperature at constant

volume. These changes were of the order of 200 kgm. for 20° intervals and could be read on the bridge with an accuracy of about $\frac{2}{3}\%$. The agreement between the two independent sets of readings was not in general as good as this, averaging about 2%. This is better than was expected at first could be obtained with the method, and is certainly
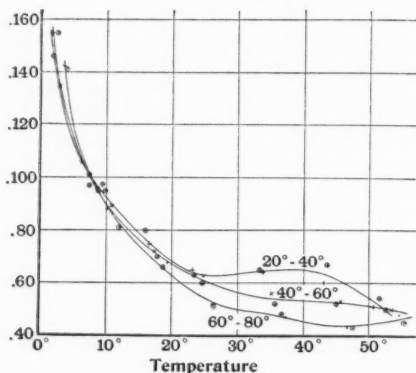

FIGURE 3. A sample set of observations on the change of volume with temperature at constant pressure. The ordinates are piston displacements in inches. Two independent sets of readings are shown on the diagram, those with the circles are the repeated set. The liquid shown here is carbon bisulphide. The accuracy for this is almost exactly the average accuracy for all twelve liquids.

much better than could have been obtained with the alternative method of determining the difference between isothermal lines for different temperatures. Figure 3 for carbon bisulphide shows a fair average of the order of agreement. A more detailed account of the order of accuracy will be given under the description of the individual liquids.

The material was now at hand for the construction of the table of volumes. Up to 5000 kgm. the volume was to be tabulated at intervals of 500 kgm., and above 5000 kgm. at intervals of 1000 kgm. The difference in the length of the pressure steps is desirable because at low pressures the volume changes more rapidly than at high pressures. The tabulation at each pressure was to be made at temperature intervals of 10°. The volume as a function of temperature at atmospheric pressure was first tabulated. This was taken from the formulas of Landolt and Börnstein, or from other sources to be described in detail under the separate liquids. The agreement between different observers, even for atmospheric pressure, is not always as close as could be

desired.   The next step was to tabulate the volume as a function of pressure over the entire pressure range at 40°, starting from the volume at atmospheric pressure and 40°.   These values were then combined with the change of volume for 20° intervals, thus giving the volume for each pressure at 20°, 60° and 80°.   To obtain the volume at the intermediate intervals of 10° a device was adopted which at the same time gave the material for determining the thermal dilatation.   The change of volume to be expected at 40° and 60° if the change had been linear with temperature over the entire range was calculated from the total change of volume between 20° and 80°.   The differences between the actual and the calculated changes of volume were plotted against temperature for each pressure of the table, and smooth curves drawn through these points.   From these curves the departure from linearity at the intermediate intervals of 10° was found, and combined with the values computed by the linear relation to give the total change of volume at the desired 10° intervals.   This method, as the method for computing the isothermal compressibility, has the advantage of giving smooth curves without smoothing off the second differences.

Thermal Dilatation.— From the table of volumes the next problem was to compute the more significant quantities of thermodynamic interest.   The first of these was the thermal dilatation, or $\left(\dfrac{\partial v}{\partial \tau}\right)_p$.   "Dilatation" is perhaps not generally used in this sense, $\dfrac{1}{v}\left(\dfrac{\partial v}{\partial \tau}\right)_p$ being more common, but it has the advantage of being the quantity which enters directly into the thermodynamic formulas.   The quantity of material to which the former differentiation refers is the unit used throughout this paper, namely the quantity which at 0°C. and atmospheric pressure occupies 1 c.c.

Evidently if the dilatation were uniform over the entire temperature range it could be found from the change of volume between 20° and 80° by dividing by 60.   The dilatation is not linear, however, but departs from linearity in a way which can be found from the curves used to determine the change of volume at 10° intervals.   The correction to the linear value is obviously to be found from the slope of the difference curve, which can be found graphically from a large drawing with sufficient accuracy.   The dilatation was determined in this way at 20° intervals, and was plotted as a function of the pressure for each of the twelve liquids.

The details of the computations for the volume at 10° intervals and of the dilatation are shown more clearly perhaps in Figures 4

and 5. The experimental values of the changes of volume at 20° in-tervals were first plotted. A represents the change from 20° to 40°, B the change from 20° to 60° (obtained by adding the change 40°–60° to the change 20°–40°) and C the change 20° to 80°. The origin was now connected to C by a straight line (this was done actually by a compu-
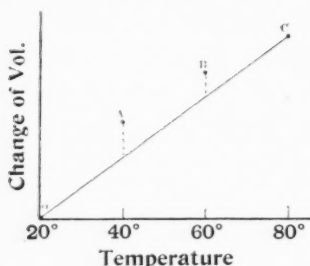

FIGURE 4. Shows the first step in finding the change of volume at inter-vals of 10° and the thermal expansion from the readings of the volumes at 20° intervals. The heavy line shows what the volume would be if the rela-tion between volume and temperature were linear.
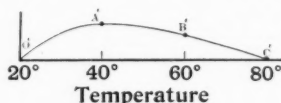

FIGURE 5. Second step in finding change of volume at 10° intervals and the thermal expansion. The point A' is the difference between the point A of Figure 4 and the straight line. The ordinates of this curve at interme-diate points, when added to the ordinates given by the straight line of Figure 4 at corresponding points, give the volume at intermediate points. The slope at A' when added to the slope of the straight line of Fig-ure 4, gives the thermal expansion at 40°, for example.

tation, not graphically) and the differences between the points 0, A, B, and C and this straight line were plotted on another diagram, Figure 5, on a larger scale. A smooth curve was drawn through these four points; from this curve the ordinates were read at the intermediate intervals of 10°, and combined with the straight line values of Figure 4 to give the volume at the temperature in question. The thermal dilatation at any temperature, 40° for example, was found by adding to the slope of the straight line 0C the slope determined graphically at the point A' of Figure 5.

This method was also applied in determining the dilatation at atmospheric pressure. An alternative method would have been by differentiating the power series of Landolt and Börnstein for volume as a function of temperature. The graphical method was thought preferable, however, because a power series may often reproduce the experimental points with greater fidelity than the slope of the experimental curve.

The dilatation, computed in this way, was transferred directly to tables, and from the tables the curves were drawn which are given later

for the dilatation. In order to save space, these tables are not given here. The thermal dilatation enters into many of the other thermodynamic quantities listed in this paper. In computing these quantities the values of the dilatation given in the tables have been used, not the values obtained from the curves given later. The same is true for all the other thermodynamic properties listed in the paper; tables were first computed for all of them before curves had been drawn for any. In this way any progressive error was avoided which might have been introduced by the use of diagrams. Although each diagram shows the property in question with as great an accuracy as is justified experimentally, it might be that if a computation involved the transference of points from one diagram to another several times, the error so introduced might finally mount up to more than the experimental error.

Isothermal Compressibility. — The compressibility, or the quantity $\left(\dfrac{\partial v}{\partial p}\right)_\tau$, was the next to be determined. This was found by a method somewhat analogous to that for the dilatation. Evidently the compressibility does not vary greatly with temperature. If the compressibility can be found as a function of pressure for one constant temperature, then the compressibility at other temperatures can be found by applying a small correction. The temperature chosen for the direct determination of the compressibility was 40°, since this was the temperature at which the change of volume with pressure had been found. The compressibility was determined graphically from a large scale drawing of the change of volume against pressure. An alternative method would have been to calculate mathematically the slope from the approximate formula for the change of volume, and then to correct this by the graphically determined slope of the difference curve. But this method would fail at the lowest pressure, 500 kgm., and at the higher pressures it did not prove necessary, because the simpler direct graphical method was sufficiently accurate.

It was now possible to correct the compressibility at 40° to the other temperatures of the tables by the use of difference curves. Let us suppose that it was desired to find the compressibility at 60°. Figure 6 represents graphically the operation which was actually performed by a computation. The curve of volume at 60° against pressure was displaced downwards (shown in the dotted line) so as to have the same origin as the curve for 40°. The difference between the curves was plotted on a large scale against pressure, and the graphically determined slope of the difference curve used as a cor-

rection to bring the compressibility from 40° to 60°. The process was performed for intervals of 20°, and the results were tabulated and plotted for the twelve liquids.

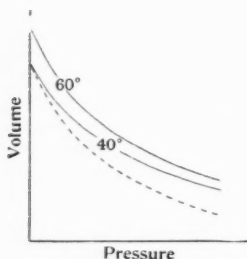The compressibility is most likely to be in error at the lower pressures, as was the dilatation. In particular, the compressibility at atmospheric pressure can be found from the method outlined above only by a wide extrapolation, and therefore is not accurate. Another method was adopted, therefore, at atmospheric pressure. Of course, the compressibilities ought to be consistent with the tables of volumes, that is, it ought to be possible to compute from the compressibility to the change of volume given in the table. The compressibility at atmospheric pressure was accordingly computed so that when combined with the compressibility at 500 kgm. it should give the proper change of volume between atmospheric pressure and 500 kgm. It was assumed in the computation that the mean compressibility between 1 and 500 kgm. was the average of the compressibilities at 1 and 500 kgm. This is not quite true, because the compressibility varies rapidly with pressure at low pressures. The value computed in this way is likely to be somewhat low. The discrepancy cannot be large, however, and this method was accepted as the best under the circumstances. The compressibility at atmospheric pressure has also been determined in a number of instances by other observers. There is not always, however, very good agreement between other observers even at atmospheric pressure, so that the compressibility at atmospheric pressure might well be the subject for further experiment in some cases. The actual disagreement at atmospheric pressure and the probable accuracy of the value finally chosen is to be given in the detailed discussion for the separate liquids.

FIGURE 6. Illustrates the method for finding the temperature correction of the compressibility.

The Work of Compression. — The mechanical work of compression was the next quantity of thermodynamic interest to be computed. This is given by the formula $\left(\dfrac{\partial W}{\partial p}\right)_\tau = -p\left(\dfrac{\partial v}{\partial p}\right)_\tau$. To find the total quantity of work done from zero up to any given pressure it is evidently necessary to integrate the derivative. This integration was performed mechanically with the integraph of the mathematical

department of Harvard University. In performing the integration there are two possible methods. We may either integrate $p\left(\dfrac{\partial v}{\partial p}\right)_\tau$ as given above, or we may integrate the equivalent expression $\left(\dfrac{\partial W}{\partial v}\right)_\tau = p$. The first involves an integration with pressure as the independent variable, and the second with volume. The first uses as the integrand the compressibility, which was obtained by computation from the experimental data, and the second uses as the integrand the pressure, which is óne of the direct experimental data. It is well known that the derivative of an experimental quantity has considerably greater error than the experimental quantity itself. The second method was adopted, therefore, using the volume as the independent variable of integration. It was a fortunate accident that the method could be used without duplication of effort, because the volume had already been plotted against pressure for another purpose. However, the direct results of the integration were not immediately available because it was necessary to obtain the work of compression as a function of pressure instead of as a function of volume. The change of variable was made with the help of the curves of volume against pressure by reading off the pressures corresponding to the given volumes.

The work of compression was found by the method outlined above at 20° intervals of temperature. It differs only slightly for different temperatures, so slightly that the difference of the work at different temperatures could not be obtained directly from the curves with as great accuracy as was necessary for computing the specific heats. In order to obtain the differences of the work with greater accuracy, an independent integration of the quantity $\Delta p\left(\dfrac{\partial v}{\partial p}\right)_\tau dp$ was performed. The symbol Δ indicates the difference of the product $p\left(\dfrac{\partial v}{\partial p}\right)_\tau$ at a given pressure for the interval 20°–40° or 40°–60° or 60°–80. These differences were taken from the tables of compressibility. The integration of the differences was performed with the integrating machine. Tests of the integrating machine showed that the accuracy of this part of the process alone was as high as $\frac{1}{10}$ %. The differences found in this way were now used in finding a better mean value for the total work of isothermal compression. For it is evidently possible with these differences to correct the work of compression at 20° or 60° or 80° back to 40°. If there were no error all these values should

agree, but of course complete agreement could not be expected. The agreement of the values corrected to 40° in this way was a few tenths of a per cent. The final value at 40° was taken as the mean of the four corrected values, and is shown in the diagrams. In the lower part of the diagrams the relation between pressure and the difference of the work of compression for 20° intervals is plotted on a larger scale.

The Heat of Compression.— The heat of compression was the next quantity to be computed. It is unfortunate that the expression, "heat of compression" is sometimes used in a sense which is not indicated by the words themselves; namely, as the rise of temperature when the pressure on a substance is increased adiabatically by the unit amount. But by no stretch of the imagination is it possible to identify a temperature with a "heat." A more descriptive name for this effect would seem to be the "temperature effect of compression." The effect was discussed under this name in the previous paper on water. By "heat of compression" we shall mean in this paper what is naturally suggested by the words, namely the heat, Q, which is given out by a unit quantity of a substance when it is compressed isothermally. It may be computed if the dilatation is known, by using the formula $\left(\dfrac{\partial Q}{\partial p}\right)_\tau = \tau \left(\dfrac{\partial v}{\partial \tau}\right)_p$. To find the total heat given out by the substance as it is compressed from the initial to the final state it is necessary to integrate this expression. The procedure was exactly analogous to that in computing the work of compression. The integration was performed first for the four temperatures. Then, in order to obtain the differences more accurately, a separate integration was made of the differences of $\tau \left(\dfrac{\partial v}{\partial \tau}\right)_p$ for intervals of temperature of 20°. With these differences the total heat at any temperature was corrected to 40°, thus giving four values for the heat of compression at 40°, of which the mean was taken for the final value at this temperature. From this final value, the values for the other temperatures were found by computing back again with the differences. The magnitude of the differences is much greater than the differences of the mechanical work, so that it was possible to plot the total heat for each temperature without confusing the diagram.

Change of Internal Energy.— From the heat of compression and the mechanical work of compression we may find at once the change of internal energy when the liquid is compressed isothermally. During compression the liquid receives work from the compressing force and delivers heat. The change of internal energy is the difference

between the work received and the heat given out.   It was computed in this way and is given in a set of diagrams (Folder 5) for the four regular temperature intervals.

Specific Heat at Constant Pressure.— Other thermodynamic quantities of a simple nature which are usually thought of as characteristic of a liquid are its two specific heats.   They also may be found by thermodynamic computation from the data given, but the accuracy is not so great as the accuracy of the other quantities. There are two methods of attack open to us here, but both of them must assume as known the specific heats at atmospheric pressure as a function of temperature.   In general, it may be shown that the characteristic equation of a substance is not sufficient in itself to determine the specific heats; we must know in addition the specific heats along some line not an isothermal.   Unfortunately, the specific heat of very few of the liquids with which we are concerned is known with accuracy as a function of temperature at atmospheric pressure. The results of different observers are often in essential disagreement. But the characteristic equation can give us the *change* of specific heats along an isothermal.   These are the results which will be tabulated in this paper, therefore, leaving for other experimenters the more accurate determination of the specific heats at atmospheric pressure. These future results may then be combined with the differences given here to determine the specific heat at any pressure.

The first method for calculating the specific heat at constant pressure is the method used in the paper on water.   It makes use of the formula $\left(\dfrac{\partial C_p}{\partial p}\right)_\tau = -\,\tau\left(\dfrac{\partial^2 v}{\partial \tau^2}\right)_p$.   Evidently in order to obtain the total change of specific heat at any pressure we must perform an integration.   The weakness of the method is that it involves the use of a second derivative, which cannot be determined with great accuracy from measurements of volume.   The method would be open to greater error if applied to these twelve liquids than in the case of water, because the dilatation varies more and more irregularly than for water.

The second method uses a cyclic process to determine the amount of heat absorbed in passing from one temperature to another at any constant pressure.   Let us imagine a liquid in the condition represented by the point A on the diagram (see Figure 7).   The liquid is now to be carried to the neighboring point D at the same pressure but at a higher temperature.   The total change of internal energy when we arrive at D is independent of the path which we have tra-

versed.   One path from A to D may be described by raising the tem-
perature from t_0 to t_1 at constant pressure.   (Path AD in Figure 7.)
In this case the liquid does a certain amount of mechanical work
against external pressure and also absorbs a quantity of heat which we
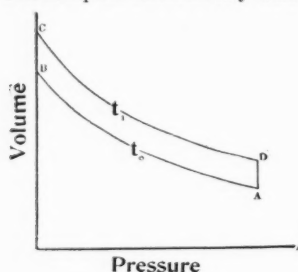can compute immediately when we know the specific heat at constant
pressure.   The external work during
this process is simply the product
of the constant pressure and the
change of volume, and may be com-
puted directly from the table of
volume as a function of pressure
and temperature.   Or we may pass
from A to D by a more circuitous
route, by lowering the pressure
isothermally at t_0 from A to B,
then raising the temperature at at-
mospheric pressure from B to C, and
then increasing the pressure isother-
mally at the final temperature t_1 to

FIGURE 7.   Shows the cycles
described in finding the specific
heat at constant pressure.

the point D.   Now the advantage of this longer route is that we know
all the quantities of energy which enter the body on the way.   The
mechanical work of compression along the isothermals from A to B
and from C to D we have already computed.   We have also found the
heat of compression along the lines A–B and C–B.   No work is done
in the expansion along the line B–C, and the heat absorbed along this
line is known if we know the specific heat at atmospheric pressure.
By comparing the inflow of energy along these different paths we are
in a position to compute either the quantity of heat absorbed along
the line A–D at constant pressure, or else the difference between this
heat and the heat absorbed along the line B–C.   This heat (or
else the difference of heat) may be plotted against the difference of
temperature between the points A and D.   The same process may be
performed at the same pressure for a number of temperature intervals,
each with t_0 as the lower limit, giving a curve of the quantity of heat
absorbed at constant pressure as a function of the temperature.   The
specific heat at any temperature is the slope of this heat curve at that
temperature.

The slope was found by a method similar to that for computing
the thermal dilatation at constant pressure.   At any temperature
the difference between the amount of heat actually absorbed and the
amount which would have been absorbed if the relation between heat

and temperature had been linear was computed and plotted against temperature. The slope of the difference curve was then found graphically, and applied as a correction to the value found on the assumption of a linear relation. The modification if C_p at atmospheric pressure is not known is obvious; a similar procedure, plotting now the difference of heats against temperature gives the difference of the specific heats at the pressure in question and atmospheric pressure. In a few cases, where the liquid boiled at a low temperature at atmospheric pressure so that it was not possible to prolong the curves to the origin of pressure, the difference between the specific heats at the pressure in question and 500 or 1000 kgm. has been given.

It is now obvious why it was necessary to know the differences of the mechanical work and the heat of compression at different temperatures with a greater accuracy than could be found from the curves obtained by a direct integration.

The units in which the specific heats are given should perhaps be mentioned because they are unusual. It is customary to give the specific heat in gm. cal. per gm. of the liquid. But this method of measuring specific heat makes no connection with the thermodynamic formulas, in which the heat is measured in mechanical units corresponding to the units of the other quantities. It was preferred here, therefore, to give the heat in units which are more unusual, but which are consistent with the other quantities, so that it is possible to substitute any of the quantities directly in the formulas without the troublesome work of changing the units. The unit of pressure is the kgm. per sq. cm., and the unit of volume the c.c. Therefore the unit of work which fits the formulas is the kgm. cm., and this is the unit in which the results have been tabulated. It is to be noticed that in making comparison with the usual values of the specific heats, it is not only necessary to change the unit of work, but the unit of quantity as well, because the amount of liquid to which this value of the specific heat is referred is not the gm., as is usual, but is the amount of liquid which at 0° C and atmospheric pressure occupies 1 c.c. In order to convert the usual value of the specific heat into these units, it is necessary to multiply by the density of the liquid at 0° and atmospheric pressure, and by 42.66, the number of kgm. cm. in 1 gm. cal.

As a check on the specific heat at constant pressure found in this way, the same quantity was computed for the first three alcohols, that is for methyl, ethyl, and propyl alcohol, by the alternative method involving the second temperature derivative of the volume which was used in the paper on water. The second derivatives were found

graphically from the curves of dilatation against temperature at constant pressure, and were integrated mechanically. The results so found agree fairly well with the values found by the other more accurate method. The magnitude of the discrepancies might be as much as 10%, but all the essential characteristics of the curve as given by one method were reproduced by the other also, such as the maxima and the minima, and the points of inflection. Of course the pressure of maximum or minimum was sometimes displaced, as was to be expected.

Specific Heat at Constant Volume.—From the specific heat at constant pressure it is now possible to compute the specific heat at constant volume by the well known formula for the difference of the two specific heats, namely $C_p - C_t = - \dfrac{\tau \left(\dfrac{\partial v}{\partial \tau}\right)_p^{\,2}}{\left(\dfrac{\partial v}{\partial p}\right)_\tau}$. This formula involves only quantities which have already been determined, so that C_t may be found immediately. The values of $\left(\dfrac{\partial v}{\partial \tau}\right)_p$ and $\left(\dfrac{\partial v}{\partial p}\right)_\tau$ used in this computation were taken from the tables, not from the diagrams. Just as for the specific heat at constant pressure, the values found in this way are the differences between C_t at atmospheric pressure and the pressure in question. The differences are such that a positive value means that the specific heat is greater at atmospheric pressure than at the pressure in question. A decreasing curve indicates, therefore, that the specific heat is increasing with increasing pressure.

In the paper on water other quantities of thermodynamic interest were plotted. These are the temperature effect of compression and the adiabatic compressibility. They may be easily calculated from the data given in this paper. While they are of interest in themselves, they do not seem to be of such fundamental importance as the quantities already listed in suggesting the possible internal mechanism of the liquid. It was felt, therefore, that to give them would unduly increase the volume of this paper, and they have accordingly not been computed.

A word seems called for as to the general character of the curves. In many cases there are slight irregularities which may very well not correspond to the actual facts, the irregularities being beyond the limit of experimental accuracy of the work. It is true that if each of these quantities were being given for itself alone, without con-

nection with other quantities, it would not have been justifiable to retain all the irregularities which some of the curves show. The reason for retaining the irregularities is that the attempt has been made to present a set of data which should be thermodynamically consistent. Let us suppose, for example, that the compressibility and the dilatation were both determined from the original tables of volumes and that they have been plotted against pressure. Both of these curves show irregularities which may be smoothed off by drawing smoother curves through the points, thus giving values of the compressibility and the dilatation which doubtless in themselves represent with greater probability the actual compressibility and dilatation. But each of these modified values for the compressibility and the dilatation will have a reflex effect on the table of volumes, which has now become inconsistent with the better values of the compressibility and the dilatation, and must therefore be altered slightly so as to be in accord with the new values. The alteration in the table necessary to accomplish this may be produced by changes less than the possible experimental error. But the point is this. Either the revised value of the compressibility or of the dilatation is sufficient of itself to completely revise the table of volume. If we are to adjust the compressibility or the dilatation we must do it so that both have the same reflex action on the table. Furthermore, all seven thermodynamic quantities must be adjusted in the same way. It is evident that this is a task of no small difficulty. To perform it, the only method seems to be a tedious one of trial and error. The labor of such an adjustment would be far beyond the labor of making the measurements with greater accuracy, and the labor had much better be so used in performing new experiments. It must furthermore be remembered that the values in the tables have been smoothed once with respect to both temperature and pressure. Any further changes would amount simply to slight changes in this smoothing; changes which were not justifiable by an examination of the data themselves but are rendered probable only by an examination of certain derived quantities. The choice has been made in this paper, therefore, to present results which may be slightly in error when taken by themselves, but which are nevertheless consistent thermodynamically.

IV. Numerical Details of Experiment and Computation.

In the detailed discussion and presentation of the results for the twelve liquids which is to follow, there will be given the experimental

accuracy to be expected for each liquid (because for some liquids the accuracy is greater than for others), and also the sources and the numerical values of the results of other observers which have been used in computing the results given here. The results taken from other work are the density at atmospheric pressure, the thermal dilatation, the initial compressibility for low pressure ranges, and the specific heats at atmospheric pressure. Unless otherwise specified, the values for the density at atmospheric pressure have been taken from the recent tables of Kaye and Laby, and the values for the thermal dilatation have been deduced from the tables of Landolt and Börnstein. In these tables the volume at any temperature is given in terms of the volume at $0°$ by a power series of the form $V_t = V_0 (1 + at + bt^2 + ct^3)$. In reproducing this expression it will not be necessary to repeat the formula each time, but merely to give the values of the three constants a, b, and c.

It has been mentioned on page 22 that in computing the changes of volume with pressure at $40°$, it was found that beyond 500 kgm. the shape of the curves was nearly the same for all twelve liquids, the only difference being in the numerical magnitudes. The constants used in the general pressure-volume formula of page 22 for the average of the twelve liquids were as follows; $\alpha = -0.0029$, $\beta = -0.0546$, $\gamma = +0.2969$, and $\delta = -0.1804$. To pass from this general formula to any one of the twelve liquids each of these four constants is to be multiplied by the same factor. This factor will be given in the following under the name of the "reduction factor."

The discussion is to be one of merely the numerical details of the measurements and the computations. The discussion of the general character of the results and their significance will be reserved until the data have all been presented.

Methyl Alcohol.— Three sets of measurements were made on this substance with three different fillings of the apparatus, the last being separated by nearly three months from the earlier two. The first measurement was of the thermal dilatation and compressibility at low pressures with the larger bulb adapted for low pressure work. The next set of measurements, made immediately afterwards, was of the compressibility and dilatation at the higher pressures with the smaller bulb for the high pressure work. The third measurement was with the high pressure bulb, and included the compressibility and dilatation over the entire pressure range, both high and low pressures. The measurements at low pressures were made, as already explained, before the piston had been upset by the higher

pressures.   The accuracy of the compressibility measurements may be estimated from the fact that the mean discrepancy of the piston displacements in the two sets of high pressure readings was 0.0035 inch, the maximum displacement being 2.07 inches.   For the dilatation, the average discrepancy in the piston displacement for a rise of temperature of 20° was 0.0011 inch, the average displacement being 0.070 inch.

In computing the volumes at atmospheric pressure the density at 15° was taken to be 0.7960, from Kaye and Laby.   The constants of the dilatation formula from Landolt and Börnstein are as follows; $a = 0.0_21186$, $b = 0.0_5156$, $c = 0.0_891^6$.   This gives for the density at 0°, 0.8100.   The quantity of methyl alcohol to which the tables and the diagrams refer weighs, therefore, 0.8100 gm.   Since the boiling point of methyl alcohol is 64.7°, the volume listed in Table II for 80° and atmospheric pressure is, therefore, merely an extrapolation by means of the formula.

The "reduction factor" by means of which the transition was made from the mathematical formula for volume in terms of pressure at 40° to the experimental curve was 1.009.

The change of volume from 1 to 500 kgm. at 40° was taken as 0.0483, following Amagat.   It should be noticed, however, that Amagat gives for the volume at 40° and atmospheric pressure 1.0438, against 1.0483 of the tables of Landolt and Börnstein.   In this work the value 1.0483 was taken as the volume at 40°, but Amagat's value for the change of volume 1–500 kgm. was adopted without correction. At low pressures (20°) the present experimental values for the changes of volume were as follows: 1–500 atmos., 0.0530; 500–1000, 0.0294; 1000–1500, 0.0242; 1500–2000, 0.0199.   The corresponding values of Amagat are 0.0480, 0.0300, 0.0239, 0.0194.   The agreement is fairly good, except for the lowest pressure interval, where as has been pointed out, the present method can only indicate the probable result by an extrapolation.   The newly published result of Richards is 0.0430 for the change of volume at 20° for an increase of 500 kgm. of pressure as against 0.0415 listed in the tables of volume.

The volume of methyl alcohol is shown as a function of pressure and temperature in Table II and in Figure 8.

The compressibility, β, of the first five alcohols has been measured by Pagliani and Palazzo,[7] who have collected their results into formulas of the type, $\beta_t = \beta_o (1 + at + bt^2)$.   Their pressure range was 1–4

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6 Pierre, Ann. chim. et.phys., **15**, 325 (1845).

7 Pagliani and Palazzo, Mem. R. Acc. Lin., **19**, 279 (1883/84).

atmospheres. Within this range the change of compressibility with pressure is negligible. The values found from their formulas (reduc-

TABLE II.

VOLUME OF METHYL ALCOHOL.

Pressure. kgm. cm.²	Volume						
	20°.	30°.	40°.	50°.	60°.	70°.	80°.
1	1.0238	1.0361	1.0483	1.0610	1.0737	1.0869	1.1005
500	0.9823	0.9909	1.0000	1.0096	1.0197	1.0401	1.0416
1000	.9530	.9607	0.9684	0.9763	0.9844	0.9929	1.0023
1500	.9276	.9347	.9415	.9481	.9549	.9621	0.9697
2000	.9087	.9151	.9213	.9271	.9331	.9393	.9456
2500	.8930	.8988	.9044	.9098	.9151	.9205	.9260
3000	.8792	.8845	.8897	.8947	.8997	.9047	.9095
3500	.8663	.8712	.8761	.8808	.8854	.8899	.8944
4000	.8551	.8597	.8642	.8687	.8730	.8773	.8814
4500	.8449	.8492	.8535	.8577	.8618	.8657	.8695
5000	.8354	.8395	.8436	.8476	.8515	.8552	.8588
6000	.8192	.8232	.8271	.8307	.8344	.8379	.8412
7000	.8053	.8091	.8129	.8164	.8196	.8228	.8262
8000	.7936	.7972	.8008	.8040	.8070	.8108	.8134
9000	.7827	.7861	.7894	.7924	.7952	.7981	.8013
10000	.7725	.7757	.7788	.7818	.7847	.7876	.7905
11000	.7634	.7663	.7693	.7724	.7756	.7786	.7813
12000	.7559	.7586	.7614	.7647	.7682	.7712	.7738

tion being made from atmos. to kgm.) at 20°, 40°, 60°, and 80°, were 0.0_3113, 0.0_3124, 0.0_3142, and 0.0_3158 respectively. The values found from the present data by the method of computation outlined

on page 29 are 0.0_3101, 0.0_3124, 0.0_3137, and 0.0_3147 respectively. The means adopted for this paper are 108, 124, 140, and 152 respectively. There are also values for the compressibility by other observers, but not under conditions so nearly comparable with those here. These values are: 0.0_3104 at $14.7°$ and 0.0_3221 at $100°$ between 8.7
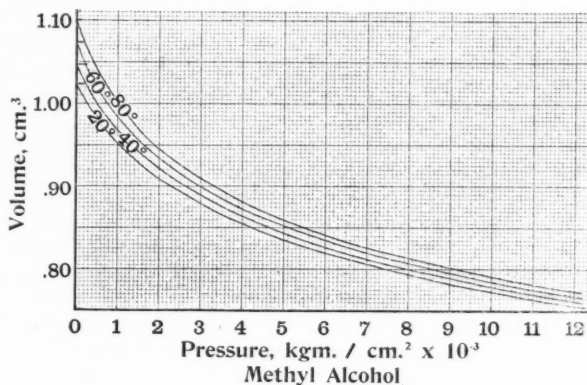

FIGURE 8.   Methyl Alcohol.   Volume at $20°$, $40°$, $60°$, and $80°$ plotted against pressure.   The lower curve gives the volume at $20°$.

and 37 atmos. by Amagat[8]; 0.0_391 at $13.5°$ and 7.5 atmos. by Grassi[9]; 0.0_3108 at $2.7°$ and 8 atmos. and 0.0_3120 at $18°$ and 8 atmos. by Röntgen.[10]   The newly published value of Richards for the compressibility at $20°$ is 0.0_3109 against 0.0_3108 adopted above.

There are a few measurements for the specific heat, C_p, at atmospheric pressure; 20.39 between $5°$ and $10°$, 20.28 between $10°$ and $15°$, and 20.76 between $15°$ and $20°$ by Regnault[11]; 22.29 between $23°$ and $43°$ by Kopp;[12] 21.56 between $5°$ and $13°$ by Lecher;[13] and 21.40 between $15.5°$ and $34.9°$, 21.82 between $19.6°$ and $45°$, 22.13 between $18.1°$ and $50.4°$, and 22.77 between $20.5°$ and $63.2°$ by von Reis.[14]

8 Amagat. Ann. chim. et phys., **11**, 520–549 (1877).
9 Grassi, Am. chim. et phys., **31**, 437 (1851).
10 Röntgen, Wied. Ann., **44**, 1 (1891).
11 Regnault, Ann. chim. et phys., **9**, 322 (1843).
12 Kopp, Pogg. Ann., **75**, 98 (1848).
13 Lecher, Wien Ber., **76**, 937 (1877).
14 von Reis, Wied. Ann., **13**, 447–465 (1881).

These values are in the units of this paper. It will be seen that the results of different observers do not agree within 5%. The results of von Reis, however, do justify us in assuming that C_p increases with rising temperature.

Ethyl Alcohol. More measurements were made on this than on most of the other substances, because it was the liquid with which the preliminary tests of the apparatus were made, but several of the early runs were not carried to completion because of accident. Measurements were made with five fillings of the apparatus. The first of the five fillings was made with the alcohol enclosed in a glass bulb, instead of in a steel one, as in the final experiments. This filling gave all the information desired at the low pressures, and also the thermal dilatation over nearly the entire high pressure range, but was terminated by polarization effects in the manganin. The polarization was found to be due to the breaking of the glass bulb, allowing the alcohol to diffuse to the coil. The readings before the break appeared should be trustworthy. The second of the five sets of measurements was of the compressibility at high pressures, and was completed without accident, but had to be discarded, for reasons that will appear later. The third set was of the dilatation and compressibility at high pressures. This also showed polarization, but not until the very end of the compressibility run. For the second and third runs a steel bulb was used, but the top was put on with soft solder. This soft solder gave way under pressure, allowing the kerosene to mix with the alcohol. The polarization probably did not occur as soon as the solder cracked, because it takes time for the alcohol to diffuse through the kerosene to the coil. The compressibility measurements of the third run are, therefore, more likely to be in error than the dilatation measurements, which were made a considerable time before the polarization appeared. Because the apparatus was the same, the second run is likely to be in error just as the compressibility measurements of the third, the polarization not having time to appear in the second run before the apparatus was taken apart. The early dilatation measurements were retained, therefore, and the early compressibility measurements discarded. The agreement of the early compressibility measurements, which presumably were made on a mixture of kerosene and ethyl alcohol, was good, 0.3%, but they were about 4% higher than the results of the final successful run. The last two of the five runs were carried through without accident, one being of the compressibility and dilatation at low pressures, and the other the corresponding measure-

ments for high pressures. For these, and for all subsequent runs, the top of the bulb was put on with silver solder.

TABLE III.

VOLUME OF ETHYL ALCOHOL.

Pressure. kgm. cm.²	Volume.						
	20°.	30°.	40°.	50°.	60°.	70°.	80°.
1	1.0212	1.0323	1.0438	1.0557	1.0679	1.0805	1.0934
500	0.9794	0.9873	0.9956	1.0044	1.0135	1.0233	1.0334
1000	.9506	.9570	.9636	0.9707	0.9781	0.9861	0.9944
1500	.9267	.9323	.9380	.9440	.9505	.9572	.9640
2000	.9081	.9131	.9182	.9235	.9291	.9349	.9407
2500	.8923	.8969	.9016	.9064	.9114	.9165	.9216
3000	.8786	.8830	.8874	.8919	.8964	.9010	.9055
3500	.8661	.8702	.8746	.8789	.8831	.8873	.8915
4000	.8545	.8586	.8628	.8668	.8708	.8747	.8787
4500	.8439	.8481	.8521	.8559	.8597	.8634	.8671
5000	.8343	.8383	.8424	.8461	.8498	.8533	.8568
6000	.8178	.8218	.8256	.8291	.8324	.8356	.8387
7000	.8038	.8075	.8110	.8142	.8171	.8200	.8229
8000	.7917	.7952	.7984	.8013	.8038	.8065	.8094
9000	.7807	.7840	.7868	.7893	.7917	.7954	.7973
10000	.7703	.7733	.7760	.7785	.7809	.7835	.7863
11000	.7606	.7633	.7659	.7693	.7713	.7741	.7765
12000	.7521	.7545	.7571	.7600	.7631	.7652	.7682

The average discrepancy of the piston displacement for a rise of temperature of 20° at constant pressure was 0.0016 inch, the mean displacement being about 0.070 inch.

The reduction factor from the mathematical formula for volume in terms of pressure at 40° was 0.9979.

The density at atmospheric pressure and 0° was taken as 0.8063. The constants of the dilatation formula of Landolt and Börnstein were $a = 0.0_21022$, $b = 0.0_3182$, $c = 0$. The values of the volume given
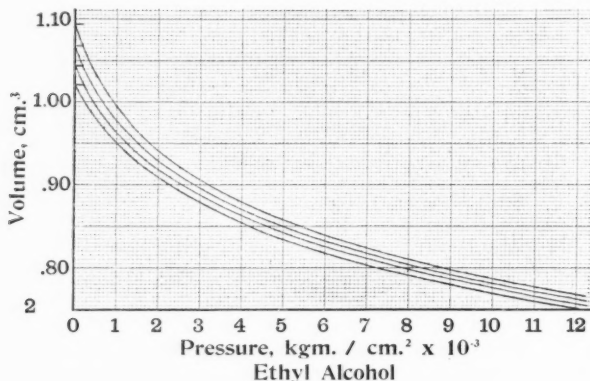

FIGURE 9. Ethyl Alcohol. Volume at 20°, 40°, 60°, and 80° plotted against pressure. The lower curve gives the volume at 20°.

by this formula are 1.0212, 1.0138, and 1.0679 at 20°, 40° and 60° respectively. We also have values of Pierre[15], which are 1.0216, 1.0448, and 1.0695 at the same temperatures respectively.

Amagat gives .0484 for the change of volume from 1 to 500 kgm. His value for the volume at 40° is 1.0442 against 1.0438 above. In the tables, 0.0484 was used as the change of volume 1–500, and 1.0438 as the volume at atmospheric pressure. At 20°, the change of volume between 1 and 500 atmos. was found to be 0.0477 against 0.0438 of Amagat. The numbers for the succeeding 500 atmos. intervals were 0.0287, 0.0236, 0.0193 against 0.0297, 0.0228, and 0.0188 of Amagat.

The volume as a function of pressure and temperature is given in Table III and in Figure 9.

The initial compressibilities at 20°, 40°, 60°, and 80°, computed as described, were found to be 0.0_3105, 0.0_3121, 0.0_3138, and 0.0_3151, respectively. The corresponding values of Pagliani and Palazzo are: 0.0_3102, 0.0_3114, 0.0_3130, and 0.0_3151. The agreement is as good as

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[15] Pierre, Am. chim. et phys., **19**, 199 (1847).

could be expected for measurements for this nature. The means shown in the curves are: 0.0_3104, 0.0_3118, 0.0_3135, and 0.0_3151. Comparison may also be made with the values of Amagat,[16] which are

TABLE IV.

C_p FOR ETHYL ALCOHOL.

Observer.	Temp.	C_p (kgm. cm.).
Regnault [17]	$-20°$	17.37
	$0°$	18.81
	$40°$	22.63
	$80°$	26.44
Sutherland [18]	$80°$	24.49
	$120°$	31.27
Zetterman [19]	$20°$	31.23
De Heen and Deruyts[20]	$40°$	20.53
von Reis	$15°.7–35°.1$	19.93
	$20°.7–45°.7$	20.78
	$18°.4–56°.0$	21.32
	$19°.8–62°.9$	21.79
	$20°.5–73°.4$	22.44

0.0_4981 at $14°$ and 0.0_3196 at $99.4°$ at a mean pressure of 22 atmos. The agreement at the lower temperature is good; the upper temperature is beyond the range.

For C_p at atmospheric pressure we have a number of values which are shown in Table IV. The results are in very bad agreement, as may be seen by plotting them. It is however, perfectly certain that on the whole C_p for ethyl alcohol increases with rising temperature.

16 Amagat, l. c. (1877).
17 Regnault, Mém. Acad., 26, 262 (1862).
18 Sutherland, Phil. Mag., 26, 298 (1888).
19 Zetterman, Akad. Afh. Helsingfors (1880).
20 De Heen and Deruyts. Bull de Belg., 15, 168 (1888).

Propyl Alcohol.— Readings were made on this liquid with two fillings of the apparatus. The first was of the compressibility and the

TABLE V.

VOLUME OF PROPYL ALCOHOL.

Pressure. kgm. cm.²	Volume.						
	20°.	30°.	40°.	50°.	60°.	70°.	80°.
1	1.0173	1.0274	1.0380	1.0493	1.0612	1.0737	1.0865
500	0.9780	0.9864	0.9948	1.0034	1.0121	1.0213	1.0320
1000	.9498	.9571	.9641	0.9710	0.9779	0.9853	0.9934
1500	.9297	.9357	.9415	.9473	.9533	.9594	.9657
2000	.9142	.9192	.9242	.9293	.9344	.9396	.9448
2500	.9011	.9055	.9100	.9145	.9190	.9235	.9282
3000	.8897	.8937	.8979	.9021	.9062	.9103	.9145
3500	.8794	.8833	.8872	.8911	.8949	.8987	.9025
4000	.8700	.8738	.8776	.8813	.8849	.8884	.8919
4500	.8612	.8650	.8688	.8723	.8758	.8791	.8823
5000	.8529	.8567	.8604	.8639	.8671	.8702	.8732
6000	.8390	.8426	.8462	.8494	.8524	.8555	.8579
7000	.8266	.8300	.8333	.8363	.8391	.8416	.8442
8000	.8163	.8193	.8223	.8250	.8277	.8302	.8328
9000	.8069	.8098	.8124	.8150	.8175	.8201	.8230
10000	.7984	.8011	.8037	.8060	.8085	.8112	.8142
11000	.7909	.7934	.7958	.7980	.8004	.8031	.8061
12000	.7840	.7864	.7885	.7905	.7928	.7955	.7982

dilatation at the higher pressures, and the second was the complete set, both compressibility and dilatation at both high and low pressures. During the last set of readings, however, the moveable plug

pinched off at a high pressure because of fatigue, so that there is only one reading for the dilatation at the two highest pressures. The agreement between the two sets at the lower pressures was good enough however, so that it did not seem necessary to set the apparatus up again merely to repeat these last two readings.
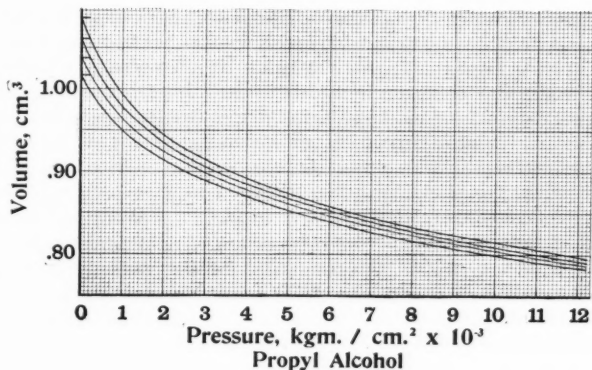

FIGURE 10.   Propyl Alcohol.   Volume at 20°, 40°, 60°, and 80° plotted against pressure.   The lower curve gives the volume at 20°.

The average discrepancy between the piston displacement of the two determinations of the compressibility at high pressures was 0.0026 inch on a total stroke of 2 inches.   The average discrepancy in the displacements at constant pressure corresponding to an increase of temperature of 20° was 0.0018 inch on a mean displacement of about 0.070 inch.

The reduction factor from the mathematical formula was 0.8726.

The density at 0° is 0.8179.   The constants of the dilatation formula are: $a = 0.0_2774$, $b = 0.0_5497$, $c = -0.0_7141$.   These values of a, b, and c are from results of Zahnder,[21] who gives for the density at 0° 0.8177, instead of 0.8179 above.   The agreement is virtually perfect.   In addition we have data by Naccari and Pagliani[22] who give for the density at 0° 0.8203, and for the volume at 20°, 40°, 60°, and 80°, 1.020, 1.042, 1.064, and 1.090 respectively, against 1.017, 1.038, 1.061, and 1.0865 adopted from Zahnder's formula above.

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21 Zahnder, Lieb. Ann., **225**, 114–193 (1882).
22 Naccari and Pagliani. Att. R. Acc. dell. Sc., **16** (Sept. 1881).

Here again it seems as if the agreement between different observers should be better.

The volume of propyl alcohol as a function of pressure and temperature is given in Table V and in Figure 10.

At 40°, Amagat gives for the change of volume between 1 and 500 kgm. 0.0432, which is the value used in the table. He gives, however, 1.0406 for the volume at atmospheric pressure against 1.0380 adopted above. It will be noticed that Amagat's value lies between those of Zahnder and of Naccari and Pagliani. At low pressures and 20° the changes of volume for successive intervals of 500 atmos. were found to be: 0.0407, 0.0245, 0.0202, and 0.0170, against 0.0399, 0.0274, 0.0211, and 0.0176 of Amagat. The agreement for the lowest pressure interval is better than on the average. Richards in his recent paper gives a change of volume between 1 and 500 kgm. considerably smaller than that used here, namely 0.0355 against 0.0393. It should be remembered that the value used in this work for 20° is founded essentially on Amagat's value for 40°, the only difference being a small temperature correction determined from these present data. The disagreement just noted means therefore, that the values of Richards are considerably lower than those of Amagat.

The initial compressibilities at 20°, 40°, 60°, and 80° were as follows; to give the value of ΔV listed in the table 0.0_492, 0.0_3103, 0.0_3118, and 0.0_3130 respectively; the corresponding values of Pagliani and Palazzo are 0.0_490, 0.0_3101, 0.0_3115, and 0.0_3133. The agreement is good. The final values taken as a fair mean were: 0.0_491, 0.0_3102, 0.0_3117, 0.0_3131. Röntgen has also measured the compressibility at atmospheric pressure. His value for 20° would be 0.0_3955, judging from a linear extrapolation from his values at 4° and 18°. Richard's recent value at 20° is 0.0_4873, lower than any other of the values given above.

For C_p at atmospheric pressure we have the following values; — 21° to +12°, 18.02 by Nadejdine[23]; 21° to 23°, 22.99 by Pagliani;[24] 21° to 90°, 23.55 by Lougiunine[25]; and from 16.5° to 42.2°, 20.54, from 20.6° to 53.4°, 21.34, from 20.4°, to 65.2°, 21.99, from 19.5° to 78.5°, 22.63, and from 20.7° to 90.8°, 23.32 by von Reis. These results also indicate a considerable rise of C_p with rising temperature.

Isobutyl Alcohol.— Measurements on this were made with two fillings of the apparatus; the first gave the compressibility and the dilata-

23 Nadejdine, Jour. Russ. Phys. Chem. Ges., **16**, 222 (1884).
24 Pagliani, N. Cim., **11**, 229 (1882).
25 Lougiunine, Am. chim. phys., **13**, 289 (1898).

tion over the high pressure range, and the second the compressibility and dilatation over both the high and low pressure ranges.   The use of isobutyl instead of normal butyl alcohol was not intended.   In ordering the chemicals, normal butyl was not specified, and it was not noticed that the substance sent was isobutyl until all the preparations had been made for a run.   This substance has the disadvantage, of not being one of the same series as the four other alcohols.   However, it makes little difference so far as the comparison of the results with those of Amagat is concerned, for Amagat did not work with either normal- or iso-butyl alcohol.   Furthermore, the use of this substance has proved very instructive in showing that a change in the structural formula changes the properties even at high pressures. It might be expected that high pressures would wipe out variations due to structural differences, but such has not proved to be the case, at least to 12000 kgm.

The average discrepancy in the piston displacements of the two determinations of compressibility was 0.0024 inch on a total displacement of 2.0 inches.   The mean discrepancy of the displacement for the thermal dilatation for 20° was 0.0008 inch on a mean of about 0.070 inch.   The agreement between the two sets of readings for the highest temperature range, 60°–80°, was virtually perfect.

The reduction factor for the mathematical formula was 0.9342.

Landolt and Börnstein's tables do not contain the requisite data for the volume of isobutyl alcohol at atmospheric pressure.   The values adopted here were obtained by Naccari and Pagliani, and are apparently the only data which have been published for this liquid. These authors have not expressed their results by a power series, but prefer instead to give the density for a considerable number of temperatures.   By interpolation from their results the volumes at 20°, 40°, 60°, and 80° were found to be: 1.0195, 1.0406, 1.0625, and 1.0880. From these results the value of Kaye and Laby for the density at 18° is reduced to 0.8165 at 0°, against 0.8162 of Naccari and Pagliani, virtual agreement.

No measurements of the change of volume of isobutyl alcohol had been made beyond a few kgm. previous to these computations, so the value obtained from the low pressure determinations of the present work was adopted.   This was 0.0484 at 40° between 1 and 500 kgm.; not at all an unlikely value, being the same as Amagat's for ethyl alcohol.   Compressibility determinations of others at low pressures have shown that isobutyl alcohol has a compressibility considerably higher than that of normal butyl alcohol, so that we are to expect a

value higher than we should predict from the behavior of propyl alcohol and a value as large as that of ethyl alcohol does not seem

TABLE VI.

Volume of Isobutyl Alcohol.

Pressure. kgm. cm.²	Volume.						
	20°.	30°.	40°.	50°.	60°.	70°.	80°.
1	1.0195	1.0300	1.0406	1.0414	1.0625	1.0744	1.0880
500	0.9751	0.9838	0.9922	1.0006	1.0093	1.0184	1.0277
1000	.9486	.9560	.9632	0.9701	0.9768	0.9840	0.9918
1500	.9268	.9330	.9391	.9448	.9505	.9565	.9630
2000	.9097	.9150	.9202	.9252	.9303	.9355	.9410
2500	.8956	.9001	.9048	.9094	.9141	.9187	.9235
3000	.8822	.8867	.8905	.8949	.8994	.9038	.9080
3500	.8705	.8743	.8782	.8823	.8867	.8908	.8947
4000	.8601	.8637	.8673	.8712	.8755	.8794	.8830
4500	.8507	.8541	.8577	.8614	.8655	.8692	.8726
5000	.8409	.8443	.8477	.8513	.8552	.8587	.8619
6000	.8269	.8301	.8335	.8369	.8403	.8433	.8463
7000	.8130	.8163	.8196	.8228	.8260	.8289	.8317
8000	.8028	.8060	.8092	.8123	.8154	.8183	.8210
9000	.7927	.7959	.7990	.8021	.8050	.8079	.8105
10000	.7832	.7863	.7894	.7924	.7953	.7980	.8007
11000	.7742	.7772	.7803	.7833	.7862	.7888	.7913
12000	.7662	.7692	.7722	.7751	.7780	.7805	.7827

unlikely. The recent work of Richards gives for the change of volume at 20° between 1 and 500 kgm. 0.0355, against 0.0344 used in the tables. The agreement is as close as could be expected when the rough nature

of the present determinations at the low pressures is considered; the agreement is better than the agreement of those values which have been taken directly from the work of Amagat.

The volume of isobutyl alcohol as a function of pressure and temperature is shown in Table VI and in Figure 11.
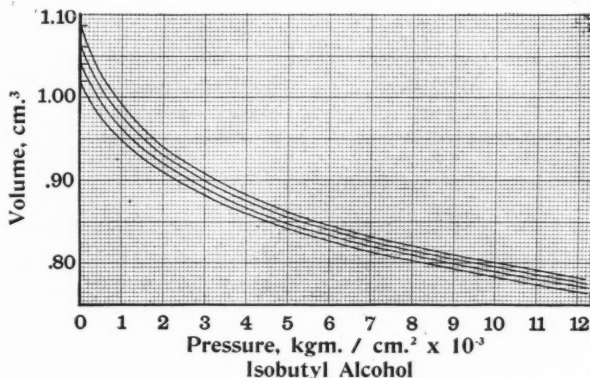

FIGURE 11.   Isobutyl Alcohol.   Volume at $20°$, $40°$, $60°$, and $80°$ plotted against pressure.   The lower curve gives the volume at $20°$.

The compressibility determinations of Pagliani and Palazzo were fortunately made with isobutyl instead of normal butyl alcohol. They give for $20°$, $40°$, $60°$, and $80°$ the values 0.0_492, 0.0_3103, 0.0_3118, and 0.0_3137.   The values required to give the values of ΔV listed in the tables are 0.0_3122, 0.0_3133, 0.0_3144, and 0.0_3164.   The discrepancy is large, too large.   Instead, however, of taking the average of the discordant results, it was preferred to retain the values consistent with the table, it being understood that the initial values between 1 and 500 kgm., both for the total change of volume and for the compressibility are probably in error.   Abnormal variations of compressibility, such as the rapid initial decrease with pressure, may possibly explain part of the discrepancy.   We have also a value of Röntgen for the compressibility at $20°$, 0.0_496, which is in very much better agreement with the value of Pagliani and Palazzo than the present value.   The recent value of Richards is practically the same as Röntgen's.

For C_p we have a larger number of measurements than we should

expect from the small number of dilatation measurements. These values are shown in Table VII. When plotted, they show considerable discrepancies. The value at $-5°$ of Nadejdine and that of Pagliani are almost certainly in error. The other points lie roughly

TABLE VII.

C_p for Isobutyl Alcohol.

Observer.	Temperature.	C_p (kgm./cm.)
Longuinine [26]	$20°–114°$	24.00
	$21°–109°$	24.94
Nadejdine [27]	$-21°–+10°$	17.70
	$16°–70°$	21.39
	$18°–98°$	23.24
de Heen and Deruyts [28]	$10°$	17.49
	$40°$	22.57
	$85°$	29.29
Pagliani [29]	$26°–30°$	23.90

on a straight line, such that C_p increases from about 15 at $0°$ to about 23 at $50°$. This is a very considerable increase.

Amyl Alcohol.—Experiments were made on this with three fillings of the apparatus; the first for compressibility and dilatation at low pressures with the large bulb, the second for compressibility and dilatation over the high pressure range, and the third for compressibility and dilatation over both ranges, high and low. The runs were all accomplished without accident of any sort.

The average discrepancy of the piston displacement for compressibility at $40°$ was 0.0019 inch on about 2 inches. The corresponding discrepancy for changes of temperature of $20°$ at constant pressure was 0.00206 inch on an mean of about 0.070 inch.

[26] Louguinine, l. c.
[27] Nadejdine, l. c.
[28] De Heen and Deruyts, l. c.
[29] Pagliani, l. c.

The reduction factor from the mathematical formula was 0.8925, showing that at high pressures amyl alcohol is one of the most incompressible of the twelve liquids.

TABLE VIII.

VOLUME OF AMYL ALCOHOL.

Pressure. kgm. cm.²	Volume.						
	20°.	30°.	40°.	50°.	60°.	70°.	80°.
1	1.0181	1.0270	1.0374	1.0476	1.0583	1.0694	1.0814
500	0.9800	0.9880	0.9959	1.0039	1.0122	1.0210	1.0304
1000	.9526	.9593	.9660	0.9724	0.9792	0.9863	0.9936
1500	.9325	.9383	.9440	.9495	.9551	.9608	.9667
2000	.9158	.9210	.9259	.9307	.9354	.9402	.9452
2500	.9015	.9064	.9107	.9149	.9190	.9232	.9277
3000	.8892	.8938	.8979	.9018	.9055	.9094	.9136
3500	.8780	.8823	.8864	.8900	.8935	.8971	.9010
4000	.8682	.8725	.8764	.8800	.8832	.8867	.8903
4500	.8593	.8635	.8673	.8708	.8739	.8772	.8807
5000	.8508	.8548	.8585	.8618	.8648	.8679	.8713
6000	.8373	.8409	.8442	.8471	.8501	.8530	.8560
7000	.8251	.8281	.8310	.8337	.8363	.8390	.8418
8000	.8149	.8176	.8201	.8225	.8250	.8274	.8302
9000	.8044	.8068	.8092	.8114	.8138	.8163	.8190
10000	.7948	.7971	.7994	.8018	.8041	.8066	.8091
11000	.7860	.7886	.7904	.7932	.7954	.7976	.8001
12000	.7782	.7803	.7826	.7854	.7882	.7905	.7926

The density at 0° and atmospheric pressure was taken as 0.8266. The constants of the dilatation formula were: $a = 0.0_289$, $b = 0.0_057$,

$c = 0.0_7118$. This formula of Landolt and Börnstein seems to be taken from Pierre.[30] It gives for the volumes at 20°, 40°, 60°, and 80° the values 1.0181, 1.0374, 1.0583, and 1.0814 respectively. We have also the following values by Pierre and Puchot[31]; 1.0187, 1.0397, 1.0610, and 1.0864. These authors give for the density at 0°, 0.817.
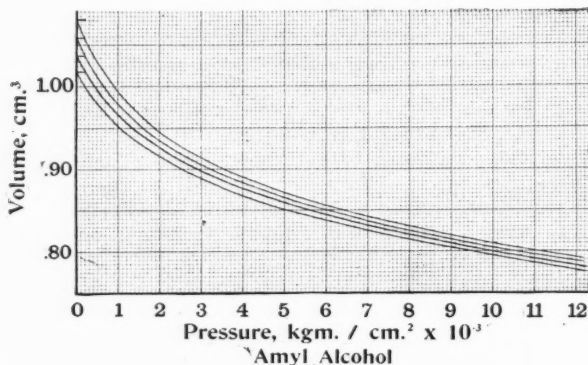
FIGURE 12. Amyl Alcohol. Volume at 20°, 40°, 60°, and 80° plotted against pressure. The lower curve gives the volume at 20°.

Zahnder[32] gives for the density at 0° 0.829, and for the constants of the dilatation formula, $a = 0.0_3919$, $b = -0.0_6461$, and $c = 0.0_7175$? Here again the discrepancies appear to be greater than they should in measurements of this character.

For the change of volume between 1 and 500 kgm. there seem to be no other data as a basis of comparison. Amagat used allyl instead of amyl alcohol for some unknown reason. The only course, therefore, was to accept the value given by this present work for the lower pressure interval, namely 0.0451. That this figure is about correct, however, is spoken for by the rather unusually close agreement of the two measurements of the piston displacement at 20°, 0.389 inch and 0.379 inch, a disagreement of 2.5%.

The volume of amyl alcohol as a function of pressure and temperature is shown in Table VIII and in Figure 12.

30 Pierre, l. c. (1847).
31 Pierre and Puchot, Ann. chim. et phys. (4), **22**, 306?
32 Zahnder, l. c.

For C_p we have the following values: 19.89 by Kopp[33] for the temperature range 26°–44°; 24.43 by Regnault[34] for the range 10°–117°; 24.51 by Louguinine[35] between 21° and 130°; and 22.97 between 20.5° and 100.1°, 23.64 between 22.2° and 111.6°, and 24.23 between 22.2° and 124.5° by von Reis. These values, which are rather more consistent than usual, show a fairly rapid increase of C_p with temperature.

Ether.—Measurements were made on this liquid with four different fillings of the apparatus. The first two, made before the method had been perfected, were neither complete because of accidents, but between them they give completely the compressibility and the dilatation over the entire high pressure range. The third set of readings was over the low pressure range; this set was repeated without refilling the apparatus. The fourth set, made with the perfected apparatus, was over the high pressure range, and was completed successfully without accident.

There were three sets of piston displacements for the compressibility at 40°. The mean discrepancy of these was $\frac{1}{2}\%$ on the maximum displacement, which is below the average in accuracy. The mean discrepancy of the piston displacements for the thermal dilatation was 0.0022 inch on about 0.070 inch, which is nearly normal.

The reduction factor from the mathematical formula was 1.104, showing that over the entire range ether remains more compressible than any of the other liquids, except ethyl chloride.

The low boiling point of ether at atmospheric pressure, 34.6°, makes it impossible to tabulate the initial properties at the higher temperatures. For this reason many of the curves start at 500 kgm. as the zero instead of atmospheric pressure.

The density of ether at atmospheric pressure and 0° was 0.7382. The three constants of the dilatation formula had the values: $a = 0.0_21513$, $b = 0.0_5236$, and $c = 0.0_7400$.[36]

The change of volume at 40° between 1 and 500 kgm. was taken from Amagat as 0.0770. Amagat gives for the volume at 40° and atmospheric pressure 1.0672 against 1.0669 of the dilatation formula above. Amagat's value for the volume at 40° and 500 kgm. was corrected, therefore, in accordance with the above. The low pressure measurements of this present work at 20° are in unusually good agreement with Amagat; 0.0665 against 0.0656 for the interval 1–500

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33 Kopp, l. c.   34 Regnault, l. c. (1862).
35 Louguinine, l. c.   36 Pierre, l. c. (1845).

atmos.; 0.0370 against 0.0379 between 500 and 1000; 0.0272 against 0.0275 between 1000 and 1500; and 0.0216 against 0.0215 between

TABLE IX.

VOLUME OF ETHER.

Pressure. kgm. cm.²	Volume.						
	20°.	30°.	40°.	50°.	60°.	70°.	80°.
1	1.0315	1.0492	1.0669				
500	0.9681	0.9790	0.9899	1.0011	1.0124	1.0247	1.0387
1000	.9363	.9445	.9530	0.9616	0.9707	0.9804	0.9906
1500	.9093	.9153	.9221	.9291	.9364	.9438	.9516
2000	.8871	.8980	.8980	.9038	.9099	.9164	.9223
2500	.8685	.8734	.8785	.8837	.8890	.8943	.8997
3000	.8530	.8576	.8623	.8670	.8718	.8765	.8912
3500	.8395	.8440	.8483	.8526	.8570	.8613	.8654
4000	.8275	.8318	.8359	.8400	.8439	.8478	.8515
4500	.8168	.8209	.8249	.8287	.8324	.8359	.8393
5000	.8071	.8111	.8149	.8186	.8220	.8253	.8284
6000	.7916	.7954	.7989	.8023	.8055	.8085	.8112
7000	.7773	.7806	.7838	.7869	.7899	.7927	.7953
8000	.7645	.7675	.7704	.7732	.7759	.7786	.7813
9000	.7525	.7554	.7580	.7606	.7632	.7658	.7687
10000	.7418	.7444	.7469	.7496	.7520	.7547	.7574
11000	.7312	.7335	.7360	.7388	.7418	.7445	.7469
12000	.7216	.7237	.7261	.7289	.7316	.7342	.7365

1500 and 2000. It may be expected, therefore, that the low pressure values of the various thermodynamic properties are rather more than usually accurate for ether.

The volume of ether as a function of pressure and temperature is shown in Table IX and in Figure 13.

For the initial compressibility at 20° and 40° we have values of Amagat[37]; 0.0_3184, and 0.0_5218 respectively.   There are also measurements by Avenarius[38] at 20° and 40°; 0.0_3191, and 0.0_3232, respec-
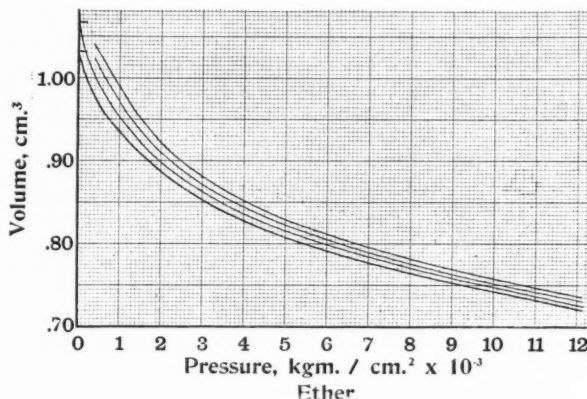
FIGURE 13. Ether. Volume at 20°, 40°, 60°, and 80° plotted against pressure. The lower curve gives volume at 20°. The curves for the higher temperatures could not be extended to the origin because of the low boiling point.

tively.   The values needed to give the changes of volume listed in the table are 0.0_3170, and 0.0_3215. The mean values finally adopted were 0.0_3184, and 0.0_3220. There are also other measurements by Grimaldi[39] and Amagat at temperatures considerably above the normal boiling point, and at accordingly increased pressures, 20 kgm. or so. It was not attempted to make connections with these values.

C_p has been measured by Regnault[40], who gives 20.97 at 0°, and 21.69 at 30°; by Sutherland[41], whose values are 27.35 at 80°, and 31.86 at 120°; and by de Heen[42], who found 32.59 at 140°, and 41.27 at

37 Amagat, l. c., (1877).
38 Avenarius, Bull. Acc. St. Pet., 10 (1877).
39 Grimaldi, N. Cim., 19, 7 (1886).
40 Regnault, l. c. (1862).
41 Sutherland, l. c.
42 de Heen, Bull de Belg., 15, 522 (1888).

180°. These values all lie roughly on a curve passing through 20.0 at 0°, 23.5 at 40°, 27.0 at 80°, 31.0 at 120°, and 36.5 at 160°. The increase of C_p with temperature is fairly rapid, and becomes more rapid at the higher temperatures.

Acetone.— Two fillings of the apparatus with this substance were made. The high pressure measurements only were made with the first filling, and both high and low pressure readings with the second. Acetone was unique among the liquids used in that it froze under pressure. This was not anticipated nor desired, since, for one thing, it made impossible measurements at the lower temperatures and higher pressures. Furthermore, the separation of the solid phase is apparently accompanied or foreshadowed by complications in the behavior of the liquid, which it was not desired to encounter at the present stage. As a consequence of the freezing, the readings at 20° run only to 8000 kgm. The curves showing the average properties of acetone over the entire temperature range all show a break, therefore, at 8000 kgm. Below 8000 kgm. the average is over the range from 20° to 80°, but above 8000 the range is from 40° to 80°.

No attempt was made to follow out the freezing curve, or to determine accurately the equilibrium pressure at any temperature. It was found, however, that at 40° the freezing pressure is about 10000 kgm. The freezing point of acetone at atmospheric pressure is given by Kaye and Laby at − 95°. This raising of the freezing point by 135° seems to be larger than any previously recorded.

Acetone also showed one other peculiarity. When the liquid was examined at the close of the second run, it was found to be of a slight rose color, and there was a small amount of a fine white precipitate. The rose color deepened in the course of several days to a dirty brown, and the precipitate appeared to increase slightly in quantity. It was thought at the time that this was a chemical reaction brought about by pressure alone, but subsequent investigation showed that the effect was doubtless due to the presence of a slight impurity of phosphorus trichloride, left from the previous run. Phosphorus trichloride when mixed with acetone and allowed to stand at atmospheric pressure was found to produce very slowly the same discoloration and precipitate as observed after exposure to pressure. The effect of pressure apparently is merely to hasten the reaction. In a subsequent experiment, in which every trace of phosphorus trichloride had been carefully removed by prolonged heating, acetone was submitted to the pressures and temperatures of the regular experiment for a day, with absolutely no trace of discoloration. Unfortunately, no examination

was made of the condition of the liquid after the end of the first run, so it cannot be told whether the effect was present then or not; probably not. In any event the error so introduced is probably very small, because not more than a very small impurity of PCl_3 could have escaped attention in the weighing. There is, however, a slight possibility that the reaction was catalytic, in which event the error might be greater. The close agreement of the two sets of readings makes this unlikely, however.

The mean discrepancy in the piston readings for compressibility was about 0.005 inch on a total stroke of 2.0 inches. The first compressibility readings were made at $40°$ The liquid does not freeze until it has been considerably subcooled, so that it was possible to cover the entire pressure range at $40°$. But in order to avoid the possibility of the liquid freezing the second time at a less degree of subcooling than at first, the second run was made at $60°$, and then reduced to $40°$ for comparison with the first run. The average discrepancy of the displacements for thermal dilatation was 0.0013 inch on an average of 0.070 inch.

The reduction factor from the mathematical formula was 1.049, showing that acetone is more compressible than the average.

The boiling point of acetone is $56.5°$, so that for this reason the initial point of the $80°$ curve is taken as 1000 kgm. The initial values at $60°$ were obtained by extrapolation, disregarding the boiling, and strictly apply only to a zero of a few kgm.

The density of acetone at atmospheric pressure and $0°$ was assumed to be 0.8136. The constants of the dilatation formula were: $a = 0.0_21324$, $b = 0.0_5380$, and $c = -0.0_888$. These constants are taken from data of Zahnder, who gives for the density at $0°$ 0.8125, and for the boiling point $56.3°$, values slightly different from those given above.

The change of volume at $40°$ between 1 and 500 kgm. was taken as 0.0541 from Amagat. His value for the volume at $40°$ and 1 kgm., however, is 1.0575 against 1.0585 given by the formula above. The probable accuracy of the low pressure measurements of acetone may be judged from a comparison of the values at $20°$ with those of Amagat. For the successive pressure intervals 1–500, 500–1000, 1000–1500, and 1500–2000 atmos. the present work gave the following changes of volume; 0.0526, 0.0308, 0.0251, 0.0208, while Amagat gives 0.0483, 0.0325, 0.0245, and 0.0196.

The volume of acetone as a function of temperature and pressure is shown in Table X and in Figure 14.

The initial compressibility at 20°, 40°, and 60° may be computed from values of Amagat[43] at 14° and 99°, between 15 and 22 atmos.

TABLE X.

VOLUME OF ACETONE.

Pressure. kgm. cm.²	Volume.						
	20°.	30°.	40°.	50°.	60°.	70°.	80°.
1	1.0279	1.0426	1.0585	1.0752	1.0929		
500	0.9829	0.9931	1.0044	1.0165	1.0297		
1000	.9553	.9638	0.9728	0.9821	0.9924	1.0015	1.0107
1500	.9307	.9385	.9463	.9541	.9619	0.9694	0.9764
2000	.9100	.9173	.9243	.9309	.9374	.9436	.9497
2500	.8927	.8997	.9058	.9116	.9173	.9229	.9285
3000	.8775	.8841	.8897	.8948	.8999	.9051	.9105
3500	.8646	.8707	.8759	.8806	.8853	.8902	.8953
4000	.8532	.8586	.8636	.8681	.8725	.8771	.8819
4500	.8430	.8482	.8528	.8572	.8614	.8657	.8699
5000	.8334	.8380	.8425	.8469	.8510	.8549	.8586
6000	.8175	.8216	.8257	.8299	.8339	.8374	.8403
7000	.8028	.8064	.8103	.8145	.8182	.8215	.8243
8000	.7898	.7933	.7969	.8005	.8039	.8071	.8101
9000			.7847	.7879	.7910	.7942	.7974
10000			.7737	.7767	.7797	.7827	.7857
11000			.7634	.7667	.7697	.7725	.7750
12000			.7546	.7583	.7614	.7638	.7657

by a linear interpolation for temperature and by assuming the variation of compressibility with pressure found here.   We obtain in this

[43] Amagat, l. c. (1877).

way from Amagat's data the following values: 0.0_3121, 0.0_3143, and 0.0_3194, respectively.   The corresponding values from the present work to give the correct changes of volume are 0.0_3120, 0.0_3146, and 0.0_3167; rather good agreement except at 60°, where for one thing the linear interpolation from Amagat's data would be accountable for
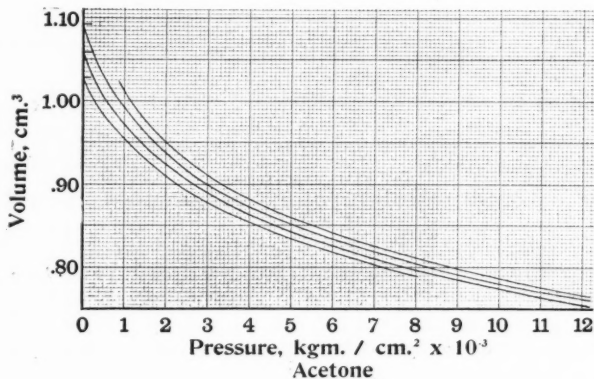
FIGURE 14.   Acetone.   Volume at 20°, 40°, 60°, and 80°, against pressure. The lower curve is for 20°.   The curve for 20° is terminated at 8000 kgm. because acetone freezes at this point.   The curve for 80° starts from 1000 kgm. because acetone boils at atmospheric pressure below 80°.

some of the divergence in the direction shown.   The values taken as the average were; 0.0_3120, 0.0_3145, and 0.0_3167.

The only values we have for C_p are by von Reis, who gives 19.43 between 16.4° and 52.6°, 19.65 between 17.6° and 60.3°, 19.68 between 18.9° and 70.2°, and 19.72 between 18.7° and 79.1°.   These data show an unusually slight increase of C_p with the temperature.

Carbon Bisulphide.— Three sets of measurements were made on this substance, the first of compressibility and dilatation at low pressures with the larger low pressure bulb, the second of compressibility and dilatation over the high pressure range with the smaller high pressure bulb, and the third of compressibility and dilatation with the smaller bulb over the entire pressure range.   All of these runs were made without accident of any sort.

The average discrepancy of the two sets of piston displacements for the isothermal compressibility at 40° was 0.002 inch, on a total stroke of about 2.0 inches.   The corresponding discrepancy for the

thermal expansion due to a change of temperature of 20° was 0.0013 inch for a mean displacement of about 0.070 inch.   As far as self consistency goes, the measurements on carbon bisulphide are among the best of the series.

TABLE XI.

VOLUME OF CARBON BISULPHIDE.

Pressure. kgm. cm.²	Volume.						
	20°.	30°.	40°.	50°.	60°.	70°.	80°.
1	1.0235	1.0357	1.0490	1.0630	1.0775	1.0928	1.0992
500	0.9865	0.9964	1.0063	1.0158	1.0256	1.0359	1.0473
1000	.9586	.9671	0.9752	0.9829	0.9907	0.9991	1.0083
1500	.9358	.9432	.9504	.9571	.9639	.9709	0.9787
2000	.9173	.9240	.9302	.9362	.9423	.9485	.9552
2500	.9018	.9076	.9133	.9188	.9244	.9299	.9357
3000	.8877	.8928	.8981	.9033	.9084	.9134	.9185
3500	.8756	.8801	.8849	.8897	.8946	.8991	.9035
4000	.8647	.8688	.8732	.8770	.8823	.8855	.8902
4500	.8548	.8586	.8627	.8672	.8714	.8752	.8786
5000	.8453	.8489	.8528	.8570	.8610	.8645	.8676
6000	.8295	.8329	.8367	.8406	.8442	.8472	.8501
7000	.8147	.8184	.8222	.8257	.8290	.8319	.8347
8000	.8022	.8061	.8100	.8131	.8162	.8191	.8220
9000	.7911	.7954	.7989	.8020	.8049	.8078	.8107
10000	.7805	.7844	.7879	.7910	.7940	.7969	.7997
11000	.7715	.7745	.7777	.7809	.7839	.7867	.7894
12000	.7638	.7658	.7682	.7710	.7743	.7772	.7795

The reduction factor from the mathematical formula was 0.9947, showing pretty nearly average compressibility. .

The density at $0°$ and atmospheric pressure was assumed to be 1.292.   The three constants of the dilatation formula were as follows: $a = 0.0_21140$, $b = 0.0_5137$, and $c = 0.0_7191$.[44]

Amagat did not measure the volume of CS_2 at $40°$ at less than 600 atmos.   The change of volume between 1 and 500 kgm. was found,
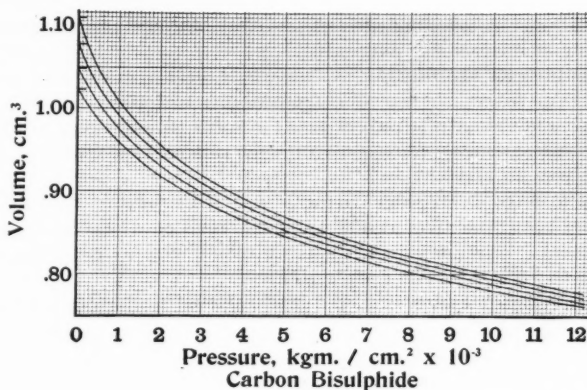
FIGURE 15.   Carbon Bisulphide.   Volume at $20°$, $40°$, $60°$, and $80°$ plotted against pressure.   The lower curve is for $20°$.

therefore, by subtracting the value found here for 500–1000 kgm. from Amagat's value for the change 1–1000 kgm., giving the result 0.0427 between 1 and 500 kgm.   Amagat's value for the volume at $40°$ and 1 kgm. is 1.0484 against 1.0490 given by the formula above.   The present low pressure determinations gave results consistently higher than those of Amagat: These values were as follows: 0.0476 (not accurate) for 1–500 atmos., 0.0295 between 500 and 1000, 0.0227 between 1000 and 1500, 0.0198 between 1500 and 2000.   For the same pressure intervals Amagat has 0.0387, 0.0277, 0.0222, and 0.0183.

The volume of carbon bisulphide as a function of pressure and temperature is shown in Table XI and in Figure 15.

The initial compressibilities at $20°$, $40°$, $60°$, and $80°$ may be found from Amagat to have the values 0.0_490, 0.0_3107, 0.0_3128, and 0.0_3149 respectively.   The corresponding values required to give the change of volume listed in the tables are 0.0_492, 0.0_3107, 0.0_3133, and 0.0_3150; good agreement.   Röntgen also gives 0.0_487 at $20°$.   The values

[44] Pierre, l. c. (1845).

shown in the curves are the values to give the correct change of volume, except at 20°, where 0.0_491 was adopted.

There are a number of measurements of C_p for CS_2. Regnault[45] gives 12.68 at −30°, 12.95 at 0°, 13.23 at 30°; Hirn[46] gives 13.13 at 30°; Sutherland [47] 14.33 at 80°, and 15.22 at 120°; and Forch [48] 13.34 at 18°.   These results are more consistent than usual, lying on a smooth curve within about 1%. C_p increases with rising temperature, the rate of increase also increasing.

Phosphorus Trichloride.— Two sets of measurements were made on this substance; the first of compressibility and dilatation over the high pressure range, the second over the entire pressure range.   Both sets of measurements were made with the smaller high pressure bulb. There was no accident.

The average discrepancy in the piston displacements for the isothermal compressibility at 40° was 0.006 inch on a stroke of about 2.0 inches.   The discrepancy in the displacement for the dilatation was 0.0011 inch on 0.070 inch, mean.

The reduction factor from the mathematical formula was 0.9335, showing that PCl_3 is somewhat less compressible than normal.

The density at 0° and 1 kgm. was taken as 1.612.   The three constants of the dilatation formula were $a = 0.0_21139$, $b = 0.0_5167$, and $c = 0.0_840$.[49]   There are also values for the volume of PCl_3 by Pierre, who gives for 20°, 40°, and 60°: 1.0231, 1.0477, and 1.0747. The corresponding values computed with the above values for the constants are 1.0234, 1.0485, and 1.0752, rather better agreement than we have come to expect.

The change of volume at atmospheric pressure between 1 and 500 kgm. was taken from Amagat as 0.0445.   Amagat gives for the atmospheric volume at 40°, 1.0483, in substantial agreement with 1.0485, given by the formula.   At 20° and low pressures, the values found for the change of volume for successive intervals of 500 atmos. were, 0.0451, 0.0263, 0.0219, and 0.0187, against the values of Amagat; 0.0396, 0.0282, 0.0224, and 0.0186.

The volume of phosphorus trichloride as a function of pressure and temperature is given in Table XII and in Figure 16.

There seem to be no other determinations of the initial compressibility at atmospheric pressure.   Accordingly, the values given in the

45 Regnault, l. c. (1862).
46 Hirn, Am. d. chim., **10**, 32 (1867).
47 Sutherland, l. c.
48 Forch, Ann. d. Phys., **12**, 202 (1903).
49 Thorpe, Jour. Chem. oc., **63**, 273 (1893).

tables are the values computed in the manner described on page 29 to give the correct changes of volume.

TABLE XII.

VOLUME OF PHOSPHORUS TRICHLORIDE.

Pressure. kgm. cm.²	Volume.						
	20°.	30°.	40°.	50°.	60°.	70°.	80°.
1	1.0234	1.0358	1.0485	1.0616	1.0752	1.0893	1.1039
500	0.9862	0.9949	1.0040	1.0136	1.0238	1.0346	1.0459
1000	.9593	.9666	0.9739	0.9816	0.9896	0.9980	1.0065
1500	.9382	.9445	.9509	.9575	.9643	.9712	0.9783
2000	.9205	.9262	.9318	.9377	.9437	.9498	.9557
2500	.9057	.9107	.9159	.9212	.9268	.9322	.9375
3000	.8926	.8973	.9022	.9072	.9123	.9171	.9220
3500	.8809	.8853	.8899	.8946	.8994	.9038	.9082
4000	.8705	.8747	.8790	.8836	.8880	.8922	.8962
4500	.8611	.8652	.8693	.8736	.8779	.8819	.8851
5000	.8521	.8560	.8600	.8641	.8682	.8720	.8757
6000	.8375	.8411	.8448	.8486	.8524	.8561	.8596
7000	.8245	.8279	.8313	.8347	.8382	.8416	.8450
8000	.8133	.8165	.8196	.8228	.8260	.8292	.8323
9000	.8029	.8059	.8089	.8120	.8150	.8180	.8210
10000	.7929	.7959	.7989	.8020	.8050	.8080	.8109
11000	.7838	.7866	.7897	.7927	.7957	.7985	.8014
12000	.7761	.7789	.7818	.7847	.7875	.7902	.7928

For C_p there seems to be only one determination, due to Regnault,[50] who finds the mean value 13.67 between 10° and 15°.

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[50] Regnault, l. c. (1843).

Ethyl Chloride.— Two sets of measurements were made on this substance, separated by thirty-six days in time, both with the smaller bulb, and both complete for compressibility and dilatation over the entire pressure range.   Both runs were entirely without accident of any kind.   The very low boiling point of this substance, 12.5°, and
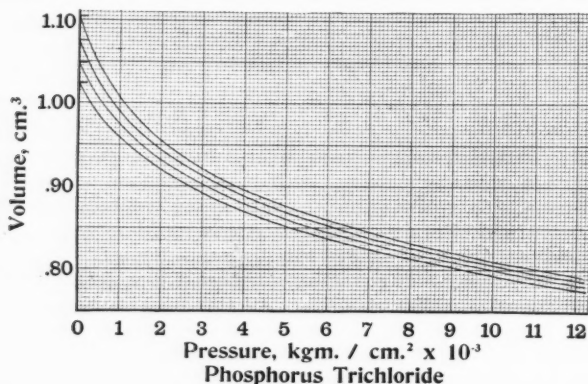
FIGURE 16.   Phosphorus Trichloride.   Volume at 20°, 40°, 60°, and 80° plotted against pressure.   The lower curve is for 20°.

its abnormally high compressibility, made slight changes necessary in the details of the manipulation.   The ethyl chloride was furnished by Kahlbaum, in sealed glass bulbs, which were accordingly exposed to an internal pressure greater than atmospheric.   The steel compressibility bulb was filled after the ethyl chloride and the bulb had been brought to 0° in an ice bath.   The steel bulb was then allowed to warm sufficiently to boil away a slight quantity of the ethyl chloride, when the capillary stem of the bulb was closed by forcing into it a small rubber stopper, considerably too large for it.   The friction of the stopper was sufficient to hold it in place against the vapor pressure of the ethyl chloride at room temperature.   The first application of a very moderate pressure by the pump was sufficient to drive the stopper into the bulb, where it remained during the rest of the measurements. In this way the filling could be accomplished without the troublesome necessity of cooling the large cylinder below 12° and maintaining it there until pressure could be applied.   The small rubber stopper was

weighed, and its weight applied as a correction to the weight of the bulb full of the chloride.   The weight was about 0.03 gm.

The piston displacement for isothermal compressibility at 40° showed a mean discrepancy of 0.0016 inch on a total of about 2.1 inches.   The discrepancy in the displacements for dilatation averaged 0.002 inch on a mean of about 0.070 inch.   The larger discrepancies were at the lower pressures; the mean above 2000 kgm. was 0.001 inch, half as much.

It has already been mentioned that ethyl chloride is so abnormally compressible that it was not possible to use the same formula as for the other eleven liquids to smooth the changes of volume at 40° for the tables.   A formula of the same type was used, but with different coefficients (see page 22).   The best values of the coefficients for ethyl chloride were found to be, $\alpha = 0.06723$, $\beta = 0.17139$, $\gamma = 0.04030$, and $\delta = -0.06261$.   The maximum differences between the observed and the calculated change of volume were $+ 0.0007$ at 3000 kgm. and -0.0024 at 9000 kgm.   The four constants were determined so that the curve passed through the experimental points at 500, 2000, 5000, and 12000 kgm.   It should perhaps be mentioned that this formula is merely an empirical expression for the change of volume over the pressure range of the experiment.   It has no theoretical significance whatever, and should not be used for purposes of extrapolation.   For instance, it is seen immediately that it predicts an impossible behavior at infinite pressure.

The density at 0° was taken as 0.9120.   The liquid boils at atmospheric pressure for every temperature within the range of the table. The ordinary dilatation formula would have been valueless, therefore, to fix the volume at any one point of the table.   The fiducial point was taken at 40° and 500 kgm. from the data of Amagat,[51] who gives 0.9951 for the volume.   The fact that the liquid boils at all temperatures of the table at atmospheric pressure has necessitated starting from 500 or 1000 kgm. as the initial point from which most of the thermodynamic properties have been computed.

The initial compressibilities given in the diagrams for 20° and 40° were taken from Amagat by interpolation and extrapolation from 22 atmos.   The values are 0.0_3163, and 0.0_3211; they correspond to pressures somewhat higher than atmospheric.

The volume of ethyl chloride as a function of pressure and temperature is given in Table XIII and in Figure 17.

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[51] Amagat, l. c. (1877).

For C_p we have apparently only one value, again due to Regnault,[52] who gives 16.80 at $-28.4°$, a temperature beyond the range of this work.

TABLE XIII.

Volume of Ethyl Chloride.

Pressure. kgm. cm.^{2}	Volume.						
	20°.	30°.	40°.	50°.	60°.	70°.	80°.
1							
500	0.9714	0.9831	0.9951	1.0075	1.0105	1.0339	1.0379
1000	.9276	0.9358	.9446	0.9544	0.9647	0.9741	0.9827
1500	.8988	.9059	.9132	.9211	.9296	.9373	.9444
2000	.8774	.8836	.8900	.8967	.9039	.9104	.9264
2500	.8596	.8652	.8709	.8768	.8831	.8888	.8938
3000	.8442	.8492	.8544	.8599	.8654	.8703	.8749
3500	.8311	.8358	.8405	.8456	.8506	.8551	.8591
4000	.8200	.8245	.8289	.8337	.8384	.8426	.8462
4500	.8087	.8129	.8172	.8217	.8262	.8301	.8335
5000	.7994	.8035	.8076	.8118	.8161	.8199	.8230
6000	.7821	.7860	.7900	.7938	.7976	.8010	.8040
7000	.7680	.7718	.7756	.7791	.7825	.7856	.7887
8000	.7561	.7597	.7633	.7666	.7699	.7730	.7762
9000	.7454	.7490	.7522	.7553	.7581	.7611	.7644
10000	.7352	.7385	.7415	.7444	.7473	.7502	.7533
11000	.7259	.7288	.7317	.7347	.7376	.7405	.7432
12000	.7176	.7199	.7225	.7254	.7286	.7314	.7336

Ethyl Bromide.— Two sets of measurements were made on this, both being with the smaller bulb and over the entire pressure range.

[52] Regnault, l. c. (1862).

An interval of forty days separated the two sets. Both were completed without accident.

The average discrepancy of the piston displacements for isothermal compressibility at 40° was 0.0025 inch on a stroke of 2.05 inches. The mean discrepancy in the displacements for dilatation was 0.0013 inch on a mean of about 0.070 inch.
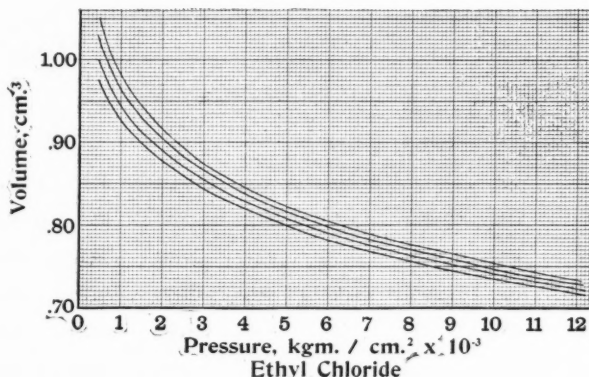
FIGURE 17. Ethyl Chloride. Volume at 20°, 40°, 60°, and 80° plotted against pressure. The lower curve is for 20°. The boiling point at atmospheric pressure is at 12°.5, so that it was necessary to take the origin of pressure as 500 kgm.

The reduction factor for passing from the mathematical formula was 1.032, indicating a compressibility somewhat more than normal.

The density at 0° and atmospheric pressure was assumed to be 1.483. The three constants of the dilatation formula were taken as $a_2 = 0.012275$, $b = 0.0_64437$, and $c = 0.0_70258$.[53] The boiling point of ethyl bromide is 38.4°. The formula gives for the volume at 20° 1.0249, and for the extrapolated value at 40°, 1.0515. Pierre also gives the volumes at 20° and 40°, 1.0275 and 1.0578 respectively. The discrepancies are large, 0.6% at 40°. In this case the preference has been given to the values of Pierre against those of Landolt and Börnstein, because Pierre actually measured the volumes at the temperatures in question, where as the formula of Landolt and Börnstein is directly applicable only at lower temperatures. Furthermore,

[53] Pierre, l. c. (1845).

Amagat's value at 40°, 1.0583, agrees much more closely with Pierre's than with that given by the formula.

TABLE XIV.

VOLUME OF ETHYL BROMIDE.

Pressure. kgm. cm.²	Volume.						
	20°.	30°.	40°.	50°.	60°.	70°.	80°.
1	1.0275	1.0418(?)	1.0578				
500	0.9788	0.9890(?)	1.0004				
1000	.9478	.9557	0.9644	0.9534	0.9824	0.9919	1.0018
1500	.9237	.9309	.9380	.9448	.9517	.9585	0.9654
2000	.9044	.9110	.9175	.9235	.9294	.9350	.9407
2500	.8885	.8950	.9011	.9066	.9120	.9170	.9218
3000	.8776	.8839	.8898	.8951	.9000	.9046	.9090
3500	.8610	.8670	.8725	.8775	.8821	.8864	.8904
4000	.8505	.8556	.8606	.8652	.8696	.8735	.8772
4500	.8410	.8455	.8500	.8543	.8585	.8622	.8657
5000	.8317	.8358	.8399	.8439	.8478	.8514	.8546
6000	.8163	.8201	.8237	.8273	.8307	.8340	.8371
7000	.8020	.8056	.8092	.8125	.8156	.8187	.8220
8000	.7900	.7935	.7968	.7999	.8028	.8059	.8091
9000	.7787	.7821	.7852	.7881	.7911	.7939	.7968
10000	.7686	.7717	.7747	.7777	.7807	.7834	.7858
11000	.7598	.7623	.7653	.7684	.7715	.7741	.7762
12000	.7521	.7546	.7572	.7601	.7633	.7659	.7677

The change of volume at 40° between 1 and 500 kgm. was taken as 0.0573 from Amagat. The values found here at 20° for successive intervals of 500 kgm., beginning at 1 kgm. were 0.0536, 0.0320, 0.0255,

and 0.0202, against 0.0492, 0.0322, 0.0248, and 0.0199 of Amagat. The agreement is rather good, except at the lowest pressure, where agreement is not to be expected. The just published value of Richards for the change of volume at 500 kgm. and 20° is 0.0446, against 0.0487 given in the table, which is essentially that of Amagat.
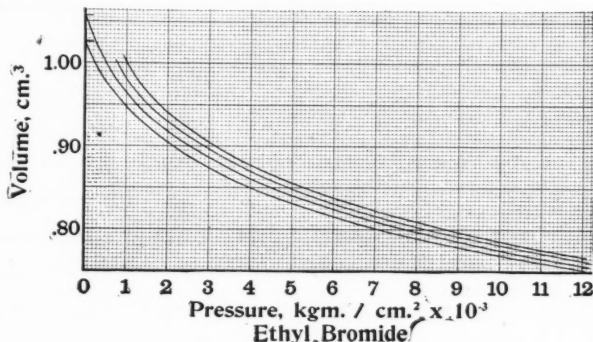
FIGURE 18. Ethyl Bromide. Volume at 20°, 40°, 60°, and 80° plotted against pressure. The lower curve is for 20°. The curves for 60° and 80° start from 1000 kgm. because the boiling point at atmospheric pressure is below 60°.

The volume of ethyl bromide as a function of pressure and temperature is given in Table XIV and in Figure 18.

When the computations of this paper were made the only value for the compressibility at low pressures was that of Amagat at 99° and a mean pressure of 20 atmos. This was too far removed from the range of this paper to justify any correction. The initial compressibilities at 20° and 40° were taken, therefore, so as to give the values of the changes of volume listed in the tables; 0.0_31248 and 0.0_31476 respectively. At 60° and 80° the compressibility is not given for pressures lower than 1000 kgm. The recently published data of Richards give for the compressibility at atmospheric pressure and 20° the value 0.0_3106, considerably lower than the value given above.

Regnault[54] gives a few values for C_p at atmospheric pressure; 14.62 between 5° and 10°, 14.42 between 10° and 15°, 14.54 between 15° and 20°. The temperature range is too small and the variations

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[54] Regnault, l. c. (1843).

too great to enable us to decide whether C_p really increases with temperature or not.

TABLE XV.

VOLUME OF ETHYL IODIDE.

Pressure. kgm. cm.²	Volume.						
	20°.	30°.	40°.	50°.	60°.	70°.	80°.
1	1.0214	1.0324	1.0438	1.0555	1.0677	1.0803	1.0935
500	0.9785	0.9880	0.9979	1.0081	1.0180	1.0276	1.0366
1000	.9502	.9584	.9665	0.9746	0.9825	0.9900	0.9969
1500	.9277	.9345	.9412	.9479	.9544	.9605	.9663
2000	.9092	.9150	.9209	.9266	.9323	.9375	.9425
2500	.8937	.8991	.9043	.9094	.9143	.9188	.9231
3000	.8802	.8851	.8899	.8945	.8988	.9028	.9065
3500	.8684	.8728	.8770	.8811	.8848	.8883	.8917
4000	.8583	.8621	.8659	.8694	.8728	.8759	.8790
4500	.8487	.8522	.8558	.8592	.8624	.8653	.8681
5000	.8394	.8429	.8463	.8496	.8529	.8557	.8581
6000	.8236	.8271	.8306	.8340	.8371	.8398	.8418
7000	.8093	.8129	.8164	.8193	.8220	.8243	.8264
8000	.7968	.8006	.8038	.8065	.8090	.8113	.8134
9000	.7856	.7902	.7922	.7945	.7967	.7989	.8013
10000	.7755	.7789	.7817	.7841	.7862	.7885	.7909
11000	.7665	.7694	.7722	.7747	.7771	.7794	.7817
12000	.7588	.7611	.7638	.7667	.7693	.7717	.7737

Ethyl Iodide.— Two runs were made on this with the smaller high pressure bulb over the entire pressure range, without accident. The mean variation of the displacement readings for compressi-

bility at 40° was 0.0020 inch on a total of 2.05 inches.   The agreement is quite perceptibly better than the average.   The thermal dilatation measurements show however, by far greater disagreement than any other of the twelve liquids.   0.0030 inch on a mean of 0.070 inch.   The discrepancy was greater at the higher temperatures;
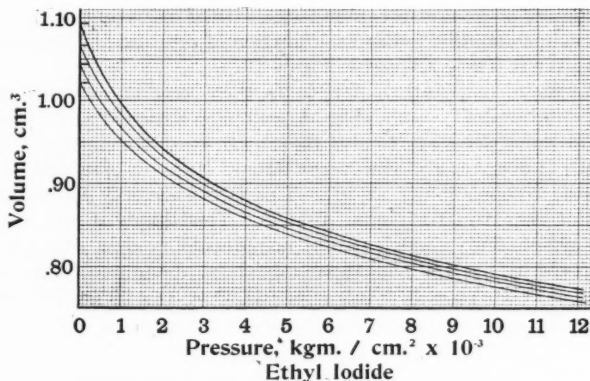
FIGURE 19. Ethyl Iodide. Volume at 20°, 40°, 60°, and 80° plotted against pressure. The lower curve is for 20°.

0.0012 inch from 20° to 40°, 0.0026 inch from 40° to 60°, and 0.0052 inch from 60° to 80°.

The reduction factor from the mathematical formula was 0.9817, showing slightly less than normal compressibility.

The density at 0° was assumed to be 1.973.   The three constants of the dilatation formula were as follows: $a = 0.0_2 1054$, $b = 0.0_6 636$, and $c = 0.0_7 1004$.[55] Pierre also gives values for the volume at 20°, 40°, and 60° respectively; 1.0232, 1.0484, 1.0749, against 1.0214, 1.0438, and 1.0677 given by the formula.   The agreement should be better.   Probably Pierre's values are better, as is shown by the agreement of Amagat's value at 40°, but Pierre does not give the volume at 80°; so the value of the formula was accordingly selected.

The change of volume between 1 and 500 kgm. was taken from Amagat as 0.0459.   Amagat gives for the initial volume at 40° 1.0486 against 1.0438 of the formula.   The low pressure determina-

[55] Dobriner, Lieb. Ann., **243**, 1–23 (1888).

tions of the change of volume at 20° gave for successive intervals of 500 atmos. 0.0509, 0.0278, 0.0233, and 0.0195 respectively, against 0.0404, 0.0289, 0.0227, and 0.0184 of Amagat. The agreement is fair, except of course for the first interval. The recent work of Richards gives 0.0370 for the change of volume at 20° and 500 kgm. against 0.0429 given in the tables. It is evident that the work of Richards and of Amagat is here in very essential disagreement.

The volume of ethyl iodide as a function of pressure and temperature is given in Table XV and in Figure 19.

When these computations were made there were no values of the initial compressibility with which to compare the results. Accordingly the value necessary to give the change of volume in the tables was used in every case. The recent data of Richards give 0.0_491 for the initial compressibility at 20°. This is considerably lower than the value shown in the curves, 0.0_4108. This simply means again that Richards finds a much smaller compressibility than Amagat.

C_p for ethyl iodide has apparently been determined only by Regnault [56]. He gives 13.19 at $- 30°$, 13.60 at 0°, 14.03 at 30°, and 14.44 at 60°. The increase with temperature is linear.

V. Discussion of Thermodynamic Properties.

In the following sections the general characteristics of the several thermodynamic functions will be discussed. The discussion will include suggestions as to what modifications it may possibly be necessary to make in our conceptions of a liquid, or what features that we have neglected at low pressures it may be necessary to emphasize at high pressures. Incidentally in the course of the discussion, suggestions will be made bearing on the theory of liquids, but any detailed examination of the problems that confront us in trying to frame a theory of liquids valid for high pressures will be reserved for section VI.

Volume.— The tables and diagrams of volume as a function of pressure and temperature have already been given, but with little comment.

One of the significant facts about the change of volume is in regard to the volume at infinite pressures, that is, the so-called volume of the molecules themselves, which is one of the quantities entering into nearly every theory of liquids. In particular, Tumlirz [57] and

56 Regnault, l. c. (1862).
57 Tumlirz, Sitz. k. Akd. Wiss. Wien, **118**, 1–39 (1909).

Tammann [58], in their recent theories, give values for the volume at infinite pressure. The values are listed in Table XVI for four of the liquids here investigated, and compared with the volumes found experimentally at 12000 kgm. and 20°. The observed value for ether at 12000 kgm. is actually less than the value predicted by either of

TABLE XVI.

Substance.	Volume.		Observed. $p=12000$.
	Calculated, $p=\infty$		
	Tumlirz.	Tammann.	$t = 20°$
Methyl Alcohol	0.6970	0.7255	0.7559
Ethyl Alcohol	0.7037	0.7380	0.7521
Ether	0.7274	0.7246	0.7216
Carbon Bisulphide	0.6881	0.7246	0.7638

these theories for an infinite pressure; and for the other liquids the observed value is close to the predicted minimum. This result serves to emphasize more strikingly a point made in the preceding paper on water; namely, that at high pressures a liquid is more compressible than we might expect from its behavior at low pressures.

One line of inquiry is worth mentioning which seemed promising before the experiments were performed. The question, suggested by such properties of the atom as the atomic re-fraction, was this; is it possible at the higher pressures to assign to each atom its own specific volume as a function of the pressure, and so compute the volume of a compound at any pressure from its chemical constitution? But an examination of the changes of volumes of the two isomers, ether and isobutyl alcohol, shows that the supposed relation does not hold. For if we compare the volumes of equal weights, that is the volume occupied by the same number of atoms, we shall find that at atmospheric pressure the ratio of the volume of ether to that of isobutyl alcohol is 1.102, and that at 12000 kgm. it has dropped to 1.038. If the above relation were true, this ratio would be unity.

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[58] Tammann, l. c., see also Korber.

The fact that the ratio is approaching unity shows that the atoms are approaching the behavior suggested above, but if they ever reach it, it can only be at pressures considerably beyond those reached here.

In Table XVII are given the average volumes of the twelve liquids between 20° and 80°. This table corresponds to the diagrams for the average between 20° and 80° of the other thermodynamic properties; it will prove useful in plotting any of the average properties against volume, which may in some cases give more significant results than when pressure is used as the independent variable, as here.

Thermal Expansion. — The mechanism ordinarily assumed in explanation of thermal expansion is as follows. Any liquid is continually striving to expand, because of the thermal agitation of its molecules. The tendency to expand is resisted by two forces, the external pressure, and the forces of attraction between the molecules. An increase in temperature means an increase in the expanding force, which results in an increase of volume. This increase of volume would be expected to be greater if the force preventing expansion were less. Now the force preventing expansion becomes less as the volume becomes greater, because the cohesional forces decrease as the volume, or the distance apart of the molecules, becomes greater, The result is that the thermal dilatation increases with increasing temperature, that is with increasing volume. In other words, $\left(\dfrac{\partial^2 v}{\partial \tau^2}\right)_p$ is positive. Furthermore, as pressure increases, the force resisting expansion increases because of the decreased distance apart of the molecules, so that we are to expect a decreased dilatation at the higher pressures.

An examination of the curves for dilatation against pressure shows that these expectations are much more nearly fulfilled as regards the behavior of the dilatation with respect to pressure than with respect to temperature.

The general tendency of the dilatation of the separate liquids (Folder I, Figures 20 to 31) is to decrease with rising pressure. The decrease is very much more rapid at the lower than at the higher pressures. But beyond this general fact the curves give only an impression of bewildering complexity, crossing and recrossing in apparent disorder at the higher pressures. It is possible to find many instances where the dilatation increases with rising pressure over a range of several thousand kilograms, ultimately, however, to decrease again. One of the most striking examples of this is the 20° curve for carbon bisulphide; other well marked examples are afforded by ace-

TABLE XVII.

AVERAGE VOLUME BETWEEN 20° AND 80°.

Average Volume between 20° and 80°.

Pressure. kgm. cm.²	Methyl Alcohol.	Ethyl Alcohol.	Propyl Alcohol.	Isobutyl Alcohol.	Amyl Alcohol.	Ether.	Acetone.	Carbon Bisulphide.	Phosphorus Trichloride.	Ethyl Chloride.	Ethyl Bromide.	Ethyl Iodide.
1	1.0621	1.0573	1.0519	1.0538	1.0498	1.085 †	1.075 †	1.0664	1.0637		1.0755 †	1.0575
500	1.0119	1.0064	1.0050	1.0014	1.0052	1.0084	1.0165	1.0169	1.0161	1.0097	1.0120 †	1.0076
1000	0.9776	0.9725	0.9716	0.9712	0.9731	0.9635	0.9830	0.9835	0.9829	0.9552	0.9748	0.9736
1500	.9486	.9453	.9477	.9449	.9496	.9305	.9536	.9573	.9583	.9216	.9446	.9470
2000	.9271	.9244	.9295	.9254	.9305	.9047	.9299	.9363	.9381	.8969	.9226	.9259
2500	.9095	.9069	.9147	.9096	.9146	.8841	.9106	.9188	.9216	.8767	.9052	.9084
3000	.8943	.8920	.9021	.8951	.9014	.8671	.8943	.9031	.9073	.8596	.8933	.8934
3500	.8803	.8788	.8910	.8826	.8895	.8525	.8800	.8896	.8946	.8451	.8757	.8801
4000	.8682	.8666	.8810	.8716	.8793	.8395	.8676	.8775	.8834	.8331	.8639	.8687
4500	.8572	.8555	.8718	.8617	.8700	.8281	.8565	.8667	.8734	.8211	.8534	.8584
5000	.8471	.8455	.8631	.8514	.8611	.8178	.8460	.8565	.8639	.8112	.8432	.8488
6000	.8302	.8282	.8485	.8366	.8467	.8014	.8289	.8398	.8486	.7931	.8267	.8327
7000	.8157	.8134	.8354	.8224	.8335	.7863	.8136	.8247	.8348	.7784	.8120	.8179
8000	.8035	.8006	.8246	.8119	.8226	.7729	.8000	.8121	.8228	.7662	.7996	.8051
9000	.7920	.7890	.8150	.8016	.8117	.7606	.7911°	.8009	.8120	.7549	.7878	.7935
10000	.7815	.7783	.8063	.7920	.8020	.7496	.7797°	.7901	.8019	.7443	.7772	.7832
11000	.7723	.7695	.7985	.7828	.7931	.7391	.7692°	.7805	.7926	.7346	.7680	.7741
12000	.7668	.7602	.7911	.7745	.7854	.7291	.7602°	.7717	.7845	.7256	.7599	.7663

† Extrapolated to 50°.

° Average between 40° and 80°.

tone and ethyl iodide. The rule, therefore, that dilatation decreases with rising pressure has many exceptions.

As regards the behavior of dilatation with respect to temperature, it is a striking fact that at the higher pressures the dilatation is usually greatest at the lower temperatures, instead of at the higher temperatures, as at atmospheric pressure. Every one of the diagrams shows this. What is more, the reversal of the effect in almost all cases takes place sharply at a definite pressure, the same for all temperatures; or in other words, the curves for the four temperatures, 20°, 40°, 60°, and 80° all cross at approximately the same point. This is exhibited still more strikingly in the curves for the average C_p of the twelve liquids (Figure 99). We have the thermodynamic formula $\left(\dfrac{\partial C_p}{\partial p}\right)_\tau = -\tau\left(\dfrac{\partial^2 v}{\partial \tau^2}\right)_p$, so that when the average value of $\left(\dfrac{\partial^2 v}{\partial \tau^2}\right)_p$ over the temperature range vanishes C_p will have a maximum. All of the curves show this maximum at the same pressure.

This universal reversal in the sign of $\left(\dfrac{\partial^2 v}{\partial \tau^2}\right)_p$ is a fact of no little interest and importance, and seems not to have been anticipated. In fact, the natural hypothesis of the contrary behavior, namely that at high pressures $\left(\dfrac{\partial^2 v}{\partial \tau^2}\right)_p = 0$, has recently been made the basis of an empirical theory of liquids by Tammann as was pointed out in the introduction. This hypothesis of Tammann is based on very plausible evidence from the data of Amagat, which seem to indicate that at high pressures $\left(\dfrac{\partial^2 v}{\partial \tau^2}\right)_p$ does vanish. But this apparent evidence from Amagat is founded on an accident, and a rather remarkable accident, as will be evident from an inspection of Figure 99 for C_p. The reversal in the sign of $\left(\dfrac{\partial^2 v}{\partial \tau^2}\right)_p$ takes place for nearly all the twelve liquids at pressures which are in the neighborhood of 3000 kgm., the maximum pressure reached by Amagat. As a matter of fact, Amagat's data do show in some cases the reversal of the effect, but the experimental error was fairly high, and Amagat himself did not credit the reversal as genuine. Only six of Amagat's liquids can yield evidence on this point, because they are the only ones for which readings were made at more then two temperatures; of these six liquids, ether, ethyl alcohol and carbon bisulphide show the reversal at 3000 kgm., while methyl and propyl alcohol and ethyl chloride show a positive $\left(\dfrac{\partial^2 v}{\partial \tau^2}\right)_p$ over the entire range.

At higher pressures there is in many cases, though not in all, a tendency for the effect to reverse again, that is, for the dilatation to again become greater at the higher temperature. The pressure of this second reversal is in the vicinity of 9000 or 10000 kgm. This fact also is indicated by the C_p curves.

A comparison of the curves for the different liquids shows a few features of interest. In the group of the five alcohols, isobutyl stands out as being the simplest, there being none of the crossing and recrossing which the others exhibit at the higher pressures. In this respect the four normal alcohols are much alike in their high pressure complications. That isobutyl alcohol should be different from the other alcohols was not anticipated before these experiments were made, since it seemed probable that at high pressure the effect of structural differences in the molecule would be eliminated. The effect of structural difference is also shown by a comparison of isobutyl alcohol and ether, since these two have the same formula, $C_4H_{10}O$. The high pressure effects are more complicated for ether. Acetone is peculiar in the wide divergence of the curves at the maximum pressure. It does not show any unusual effects in the neighborhood of the freezing point. It will be seen later that the specific heats are the quantities most susceptible to irregularities at the freezing point. Carbon bisulphide is remarkable for the curve at 20°, which shows a large increase of dilatation between 6000 and 9000 kgm., and also in this region shows a much greater dilatation than the curves for the higher temperatures. Phosphorus trichloride is the only one of the twelve liquids which behaves approximately as had been expected, since it shows little irregularity at the high pressures, and $\left(\dfrac{\partial^2 v}{\partial \tau^2}\right)_p$ nearly vanishes. The curves for the three ethyl halogen compounds do not show any particular progressive change of character such as one might expect, except with regard to the pressure at which $\left(\dfrac{\partial^2 v}{\partial \tau^2}\right)_p$ reverses in sign. This is shown best on the diagram for C_p. The pressure for reversal is lower than for most of the other liquids, and becomes less as the molecular weight of the compound increases. This may be because the increased molecular weight produces an increase in the cohesional force of attraction, and a consequent increase in the internal pressure, with the same effect as an increase of the external pressure. Ethyl iodide is remarkable for the low value of the dilatation at 80° at 6000 kgm. The minimum as 0.00017, and is lower than for any of the other liquids at the highest pressures.

It is evident that in order to explain these complicated facts we shall have to give up the simple picture of things that led us to expect the dilatation always to increase with increasing temperature and to decrease with increasing pressure. A natural way of modifying our conceptions so as to make room for these effects would seem to be as follows. We are to think of the molecules as having complicated shapes, or what for our purposes would amount to the same thing, of being surrounded by fields of force different in different directions. This concept does not seem to be a forced or an unlikely one; it must certainly be the fact for liquids which eventually crystallize under pressure, and for liquids which do not crystallize it is hard to conceive how an assemblage of atoms with unlike chemical affinities can coalesce into a molecule identical in all aspects. The effect of pressure on such an assemblage of molecules may be somewhat as follows. As the molecules are crowded closer together, the localized centers of force on the corners and edges play an increasingly individualized part, so that for small volumes we can no longer regard the molecules as centers of force and the cohesional force as a function of the mean distance apart of the molecules, but the orientation of the molecules with respect to each other begins to have its effect. Now we suppose that the natural tendency of the molecules in a liquid under normal conditions is to arrange themselves at haphazard with relation to each other. But as the constraints increase with decreasing volume, the characteristic shape compels an arrangement not entirely at haphazard, but such that the molecules fit into each other to some extent. Now it is evident that with the increasing orderliness of the arrangement of the molecules the relative positions of the localized centers of force will change. What is more, it is conceivable that the change in position of the force centers will be such that on the average the mean attraction between the molecules shall decrease with decreasing volume instead of increasing as is usual. Still more would this be true if there are centers of both attraction and repulsion in the molecule, as seems very likely from our present views of the electrical nature of matter. In this case we should expect the greater dilatation to be at the smaller volumes, because the cohesional force is less. But since the smaller volumes correspond to the lower temperatures, we have the effect already met, namely, that the dilatation is greater at the lower temperatures. The explanation of the sometimes increasing dilatation with rising pressure is similar. With increasing pressure the molecules may be forced to assume positions more regular in arrangement, of less volume, and of less average attractional

force also. The number of possible positions which the molecules may assume in this attempt to adapt themselves to the diminished space at their disposal may evidently be very great with molecules of at all complicated shapes, so that there is here the possibility of such very complicated dilatation curves as we actually have.

Another possible explanation which in the end amounts to very much the same thing for some purposes, is that of association. If we suppose that association takes place with decrease of volume, and that the amount of association is increased with increasing pressure, and is decreased with rising temperature, then we have also the possibility of decreasing dilatation with rising temperature and of increasing dilatation with rising pressure. In this case the phenomena are essentially similar to those of solidification under pressure of a mixture of different liquids. Such a case has already been investigated for kerosene, which shows the same general features as above. The phenomena for kerosene are much simpler than for these liquids, however. It is evident that one simple association (such as single to double molecules) is not sufficient of itself to explain the facts, but if we assume several associated molecules of varying degrees of complexity, and that the relative numbers of these change with pressure and temperature, the explanation would account for several of the facts actually found. But reasons will be given in the next section, for supposing that association cannot have a very large part in the phenomena at high pressures.

We now turn our attention to Figure 32, which gives in one diagram the average dilatation between 20° and 80° for all twelve liquids. The origin of each of these curves has been displaced downwards one unit with respect to the one above it. The origin is so located that the value of the thermal dilatation for each of the liquids at 12000 kgm. is between 0.0002 and 0.0003. The scale of the drawing is indicated at the side. The immediately striking feature is that the curves are nearly equi-spaced at the higher pressures. Approximate equal spacing of the curves would of course be a consequence of their all approaching zero, but this is not the entire effect by any means. For instance, the ratio of the dilatation of ether to that of amyl alcohol at low pressure is 1.50 while at 12000 kgm. pressure it has dropped to 1.03. (In the computation for ether, the initial dilatation at 20° was used.) This is only the first example of many we shall meet tending to show that at high pressures liquids lose the individual differences which characterized them at low pressures, and become more alike.

The very gradual change of dilatation with pressure at the high

pressures was also a surprise.   The grand average for the dilatation at 12000 kgm. for the twelve liquids is 0.00025, about 40% more than that of mercury at atmospheric pressure and much higher than for any solid except possibly gutta-percha.   It is ten times as great as that of aluminum, for example.   The very slow change of dilatation

TABLE XVIII.

PRESSURE AT WHICH THE THERMAL EXPANSION IS TWICE AS LARGE AS IT IS
AT 12000 KGM.

Substance.	Pressure. kgm. cm.^{2}	Substance.	Pressure. kgm. cm.^{2}
Methyl Alcohol	2150	Acetone	2900
Ethyl "	2000	Carbon Bisulphide	2900
Propyl "	2250	Phosphorus Trichloride	2200
Isobutyl "	1850	Ethyl Chloride	2750
Amyl "	2080	Ethyl Bromide	3100
Ether "	2750	Ethyl Iodide	2400

with pressure is shown in Table XVIII, giving the pressure at which the dilatation has twice its value at 12000 kgm.   The table shows that between atmospheric pressure and 2400 kgm. (on the average) the dilatation falls to about 0.4 its initial value, while over a further pressure range four times as large it falls off only an additional 50%. From these data it would appear that the dilatation must remain very considerable for pressures far in excess of those reached here.   The approximate equality of the pressures for the twelve liquids at which the dilatation is double its value at 12000 kgm. indicates that the liquids behave similarly over much the greater part of the pressure range.

The curves in general fall with increasing pressure, but all the alcohols show a tendency to become stationary or to rise; while carbon bisulphide shows an extended stationary region between 6000 and 10000 kgm. but beyond 10000 its curve drops with unusual steepness.

The four normal alcohols show a dilatation continually decreasing

with increasing molecular weight.   But isobutyl alcohol shows the
effect of its different structure by a higher dilatation than its position
in the series would indicate.   A comparison of isobutyl alcohol with
ether, its isomer, shows that although initially the dilatation of ether
is greater, at 12000 kgm. it has become less.   This emphasizes again
that the structure of the molecule continues to play a part even at
high pressures.   It is not to be wondered at in view of the suggested
explanation of the complicated nature of the dilatation curves.   For
molecules of the same atomic formula, but of different structure,
are to be thought of as possessing different shapes, and it is at high
pressures that the effect of shape is greatest.

   Isothermal Compressibility.— The isothermal compressibility is
shown in Folder II; the values for the liquids separately at 20° inter-
vals in Figures 33 to 44, and in Figure 45 the average results over the
entire temperature range are collected into a single diagram for the
twelve liquids.

   The curves require a word of explanation.   Up to 4000 kgm. the
curves for each liquid are drawn for the four different temperatures,
but at pressures higher than 4000 kgm. the curves would be so close
together, sometimes crossing each other, that it would have been very
confusing to draw them on the same scale.   Therefore, at higher
pressures, the only complete curve given is for 40°, while in the upper
part of the diagram are shown on a larger scale the differences between
the compressibilities for 20° intervals.   The zero of these difference
curves is drawn as a heavy line.   Negative ordinates of the difference
curve 20°–40° indicate that the compressibility is less at 20° than at
40°; positive values for the difference curve 40°–60° indicate a greater
compressibility at 60° than at 40°, and similarly positive differences
60°–80° mean a greater compressibility at 80° than at 60°.   To find
the compressibility at 20°, one adds to the value obtained from the
40° curve the ordinates of the difference curve 20°–40° (this ordinate
is usually negative); the compressibility at 60° is found by adding to
the ordinate of the 40° curve that of the 40°–60° curve, and the com-
pressibility at 80° by adding to that at 60° (obtained as above) the
ordinate of the 60°–80° curve.   A larger compressibility at 20° than
at 40° is indicated by the difference curve 20°–40° rising from below
and crossing the axis, while a smaller compressibility at 60° than at 40°
is similarly shown by the curve 40°–60° crossing the axis from above.
The mutual crossing of the difference curves, from this point of view,
is not especially significant; it is the crossing of the axis that counts.
The meaning of the mutual crossing of the curves 40°–60° and 60°–80°,

for example, would be that over the temperature range 40°–80°,

$$\frac{\partial^2}{\partial \tau^2}\left[\left(\frac{\partial v}{\partial p}\right)_\tau\right]_p = 0.$$

The general behavior of the compressibility that one is prepared to expect from experiments at low pressures is a decrease with increasing pressure, and an increase with increasing temperature. The familiar conception of a liquid due to van der Waals is competent to explain this. The difference between the free space open to the molecules for their temperature vibrations and the total volume of the liquid is equal to the volume of the molecules themselves, or else to a small multiple of it. When pressure is increased, therefore, the free space diminishes much more rapidly than the total volume. Now we may suppose the pressure exerted by a liquid to be due in large measure to the bombardment of the walls by the temperature agitation of the molecules. The more frequent the collisions, the greater the pressure. Now at constant temperature, the number of collisions is inversely as the free space. At higher pressures, that is smaller volumes, a given diminution of total volume implies a greater diminution of the free volume than at low pressures, and therefore a greater increase of pressure. So that at small volumes (high pressures) a given decrease of volume carries with it a greater increase of pressure than at larger volumes (lower pressures), or in other words, the compressibility decreases with rising pressure. The increase of compressibility at higher temperatures is to be explained in the same way. At higher temperatures (constant pressure) the volume is greater and we expect greater compressibility. This however, is not the only element involved in the change of compressibility with temperature; there is also a temperature effect as such. It was found in the paper on water that, at equal volumes, the compressibility was always less at the higher temperatures. The reason is evidently the more rapid agitation of the molecules. At equal volumes, a given decrease in the total volume, and so of the free volume, will produce the same proportional increase in the number of impacts at high and low temperatures, but at high temperatures each impact involves a greater change of momentum, with the result that at the higher temperatures a given decrease of volume produces a greater increase in pressure, which means a lower compressibility.

A detailed examination of the curves shows that these expectations are justified to a rather greater degree than was the case for the thermal dilatation. The compressibility decreases with rising pressure for all twelve liquids at 40°. A careful analysis of the difference

curves will show that this is also the case for the other three tempera-
tures, with a single exception. For carbon bisulphide, between
11000 and 12000 kgm. there is an increase of compressibility from
0.0_3101 to 0.0_3102 at $60°$, and from 0.0_3103 to 0.0_3105 at $80°$. The
change is very small and may well be due to experimental error. The
difference curves show as bewildering small variations with tempera-
ture as the thermal dilatation curves, so that it is hopeless to try to
explain them in detail at this stage of our knowledge. It would seem,
however, that an actual reversal of the effect, that is, a smaller com-
pressibility at a higher temperature, does not occur so often as was
the case for the dilatation. The reversal of the dilatation was uni-
versal for all liquids and took place between 1000 and 3000 kgm.
But the reversal of the compressibility, indicated by the difference
curve crossing the axis, is sporadic in occurrence, and only once occurs
for all temperatures simultaneously.

Comparison of the curves shows some points of interest. The first
three alcohols show a slight kink; propyl alcohol at 3000 kgm., ethyl
at 1100, and methyl possibly at a somewhat lower pressure. Amyl
alcohol apparently has lost the kink. These four alcohols show in
rather desultory fashion for at least one temperature the temperature
reversal at high pressures. Isobutyl alcohol, as we expect, shows
the effect of structural variation by curves of different character from
the other four alcohols, in that they show no reversal, but decrease
with fair regularity under increasing pressure. Isobutyl alcohol is
also remarkable for the extremely rapid initial drop of compressi-
bility with rising pressure. Ether, the isomer of isobutyl alcohol,
still further shows the importance of the structure of the molecule;
the difference curves for ether show reversal at high pressures, and
are also more widely separated than the curves for isobutyl alcohol.
The last six liquids show a somewhat greater temperature effect on
compressibility than the first six. Acetone shows a strange maximum
in the difference curve between 4000 and 5000. Carbon bisulphide
shows greater variations at the highest pressures than any other
liquid (it will be remembered that the dilatation curves also show
abnormally great variations), and a reversal of the effect at 9000 kgm.
simultaneous for all temperatures. This simultaneous reversal is
shown by no other liquid, and reminds one of the dilatation. Phos-
phorus trichloride shows no marked features; the compressibility
curves are not so simple as the dilatation curves. The halogen com-
pounds do not show any marked similarities. Ethyl chloride is with-
out particular features. Ethyl bromide has a very pronounced

separation of the curves for 20° and 40° at 4000 kgm., while ethyl iodide shows a similar, but smaller separation between the 20°–40° and also the 40°–60° curves. The halogens all show reversals at the high pressures.

The occasional reversal of compressibility with temperature, that is, a smaller compressibility at a higher temperature, has ready explanation if we adopt the hypothesis of molecules with shape. We have seen that in this event, because of the varying completeness with which the molecules interlock, it may sometimes happen that the increase of volume with temperature results in a decrease of the free space open to the thermal agitation of the molecules. In this case the compressibility is less at high temperatures than at low. The same argument would admit also the possibility of compressibility increasing with increasing pressure if the effect of pressure is to produce a better fitting together of the molecules and so greater free space. It may be, therefore, that the effect found for carbon bisulphide is genuine, and not to be explained away by experimental error.

As a general rule, the result found for water applies to these twelve liquids also, namely that compressibility when plotted against volume is less at the higher temperatures. There are, however, a few exceptions. Carbon bisulphide and ethyl chloride, for example, show a reverse effect at the higher pressures. A possible explanation of this is to be found in the opposition of two effects. In general we think of the effects of lowering the temperature and of increasing the pressure as the same, namely to increase the degree of interlocking of the molecules. If now we compare two states of the liquid, each occupying the same volume, but one at a higher temperature than the other, we see that the high temperature condition differs from the low in that the molecules are less interlocked so that they have less free space at their disposal. An increase of pressure will tend to produce a smaller change of volume at the high temperature therefore, because of the smaller free space which the molecules possess. But on the other hand, an increase of pressure will tend to produce a greater change of volume because the effect of increased pressure is to increase the amount of interlocking, and so to decrease the volume. As one or the other of these effects predominates, we shall have smaller or greater compressibility at the higher temperatures with constant volume. We have seen that the compressibility is usually smaller.

We turn now to the diagram (Figure 45) in which are collected

the average of the results for all twelve liquids. As for the curves of thermal dilatation, the zeros of the successive curves are displaced

TABLE XIX.

CHANGES OF COMPRESSIBILITY AND THERMAL EXPANSION PRODUCED BY PRESSURE.

Liquid.	Compressibility, κ.				Dilatation, δ.			
	$\dfrac{\kappa_1}{\kappa_{12000}}$	$\dfrac{\kappa_{1000}}{\kappa_{12000}}$	$\dfrac{\kappa_{6000}}{\kappa_{12000}}$	κ_{12000}	$\dfrac{\delta_1}{\delta_{12000}}$	$\dfrac{\delta_{1000}}{\delta_{12000}}$	$\dfrac{\delta_{6000}}{\delta_{12000}}$	δ_{12000}
1	18.4	8.2	2.20	0.0_574	4.29	2.76	1.23	0.0_3298
2	13.7	7.4	2.02	81	4.50	2.73	1.30	268
3	15.8	7.8	1.94	70	4.80	3.06	1.33	237
4	16.6	6.3	1.68	86	4.15	2.62	1.17	275
5	14.4	7.1	1.88	74	4.40	2.84	1.30	240
6		7.7	1.62	96		3.65	1.32	248
7		7.3	1.85	87		3.27	1.35	282
8	13.8	6.3	1.82	87	5.47	3.16	1.31	262
9	14.2	7.1	1.81	80	4.84	2.83	1.31	278
10		8.4	1.78	90		3.44	1.37	267
11	14.9	8.3	1.87	82		3.46	1.33	260
12	14.9	7.2	1.89	81	4.86	3.15	1.22	248
Water	4.9	3.7	1.64	89	1.00	1.00	1.00	400
Kerosene			1.82	87			1.14	280

one square with respect to each other. The origin of each curve is so situated that at 12000 kgm. the compressibility has approached to within less than one unit of zero. Thus, the compressibility of ethyl alcohol at 12000 is 0.0_581.

The most striking feature is that the curves become nearly equi-spaced at the higher pressures. This appearance of increasing equality of behavior is not an illusion due to the approach of all the curves to

zero, but it is real, as shown by the fact that the variation in the ratios of the initial compressibilities of the liquids to each other is greater than the variation in the ratios at 12000 kgm. The increasing equality at high pressures is also made more strikingly visible to the eye by noting on the diagram at what pressure the compressibility is equal to $0.0_4 20$. For all the twelve liquids except propyl, isobutyl, and amyl alcohol this pressure is between 4000 and 5000 kgm., and for the alcohols it is not far removed. This is the same sort of thing that we have seen to hold for the dilatation curves.

The compressibility curves are, however, quite different from the dilatation curves in several respects. The effect of pressure is very much greater in decreasing the compressibility than in decreasing the dilatation. Furthermore, the decrease of compressibility at the higher pressures continues to be more rapid than that of the dilatation; both the initial and the final relative rates of change are more rapid for the compressibility than for the dilatation. This is shown in Table XIX. In the second and sixth columns of this table the relative changes of compressibility and dilatation are given over the entire pressure range. The change is about four times greater for the compressibility than for the dilatation. The fourth and eighth columns show that the change between 6000 and 12000 is greater for the compressibility than for the dilatation. In other words, the dilatation comes much nearer to approaching a finite asymptote than the compressibility. This is not what was expected at first. It was thought that at high pressures the molecules would be squeezed into virtually perfect contact, that the compressibility would be provided for by the compression of the molecules, but that under these conditions the dilatation would practically vanish. The exact reverse has turned out to be the case. The data previously obtained for water and kerosene have also been included in the table. At high pressures kerosene behaves much like the other liquids. Water is nearly normal at high pressures as regards compressibility, but is abnormal over the entire range with respect to temperature effects.

The compressibility of these liquids at 12000 kgm. may be compared with the compressibility of metals under ordinary conditions. For mercury the value is about $0.0_5 39$, and for iron $0.0_6 58$. The average compressibility of these liquids at 12000 kgm. is therefore, about twice the initial compressibility of mercury and about fourteen times that of iron. The average dilatation at 12000 approaches more nearly to that of mercury, being about 40% greater, but is farther

removed from the dilatation of iron, being about 20 times greater. The difference between compressibility and dilatation is further accentuated by the fact that the compressibility of iron is nearly as low as that of any solid, while there are a number of solids with a smaller dilatation. There seems, therefore, to be more difference between a solid and a liquid with respect to thermal expansion than with respect to compressibility.

Pressure Coefficient.— No diagrams have been given for this quantity, but it is nevertheless worth some discussion, because of the part it has played in previous theoretical discussions. This so-called "pressure coefficient" is the thermodynamic quantity $\left(\frac{\partial p}{\partial \tau}\right)_v$, the change of pressure when the temperature is raised one degree at constant volume, and is mathematically equivalent to the ratio of dilatation to compressibility $\left(\frac{\partial p}{\partial \tau}\right)_v = -\left(\frac{\partial v}{\partial \tau}\right)_p \bigg/ \left(\frac{\partial v}{\partial p}\right)_\tau$. It has been proposed as an empirical law by Ramsay and Young that the pressure coefficient is a function of the volume only. That is, if the pressure coefficient is plotted against volume, the curves for different temperatures will fall together. The experiments of Ramsay and Young covered a wide temperature range, but a comparatively low pressure range, since their chief concern was with the relations between a liquid and its vapor, and their pressures seldom exceeded the critical pressure, a matter of a few hundred atmospheres. Amagat, in his discussion of his own results for liquids up to 3000 atmos., has devoted considerable attention to the pressure coefficient. One of his results was that the pressure coefficient is approximately independent of temperature at constant volume, but does nevertheless show small consistent variations, which Amagat was unwilling to ascribe to experimental errors. The coefficient of different substances may increase or decrease with rising temperature, or show still more complicated variations. The coefficient increases with decreasing volume, that is with increasing pressure. Tammann, however, in his recent empirical theory of liquids for high pressures, has concluded from an examination of Amagat's work that the variations which Amagat found in the pressure coefficient do not exceed the possible experimental errors. Tammann has accordingly taken as one of the fundamental hypotheses of his theory the assumption that the pressure coefficient is a function of the volume only.

The discussion of the pressure coefficient to be given here has for its only purpose to show that at high pressures, whatever the facts

may be at low pressures, there is absolutely no ground for the assump-
tion that the coefficient remains independent of the temperature.
This was shown to be the fact in the previous paper on water, but the
argument lost force because water is abnormal.   However, for none
of the twelve liquids of this paper is the relation even approximately
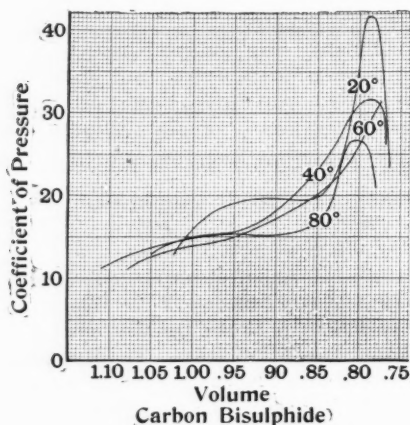
FIGURE 46.   The pressure coefficient of carbon bisulphide plotted against
volume.   The diagram shows that at high pressures the pressure coefficient
is a function of temperature as well as of volume.

satisfied.   It is not necessary to show curves for all twelve liquids
in order to disprove this one point.   The data are at hand so that any
one may make a complete test for himself.   A single diagram, chosen
at random, is sufficient to show that the proposed relation breaks
down completely, as indeed one would expect it to in view of the
complications of compressibility and dilatation.   Figure 46 shows
this for carbon bisulphide.   It speaks for itself.

Work of Compression.— The mechanical work of compres-
sion is shown in Folder III; Figures 47 to 58 are for the liquids
separately, and Figure 59 shows the average between 20° and 80° of
all twelve liquids together.   The difference of the work for different
temperatures is so nearly the same that the differences could not have
been read accurately directly from the curves.   The course was
adopted, therefore, of plotting the work at 40° only, and in the lower

part of the diagram giving on an enlarged scale the difference of the work for intervals of 20°.

The curves for the separate liquids do not require much comment. The difference curves are universally positive; that is, it is always true that more mechanical work is expended when a liquid is compressed to a given pressure at a high temperature than at a lower one. Beyond this, however, there do not seem to be many common features. The curves show irregular and apparently unrelated variations, but the irregularities are not so great as for the dilatation or the compressibility. Of course this was to be expected, because the curves are essentially integral curves.

Three of the alcohols, methyl, ethyl, and amyl, show similar difference curves. Ether and isobutyl alcohol, isomers, are unlike, as we have found them before. The difference curve 20°–40° for carbon bisulphide shows the effect of the abnormally high compressibility at 20°, which we saw previously, and the three ethyl halogens show similarities. Other variations in the difference curves are not particularly illuminating.

Figure 59, combining the average results for the twelve liquids, is of more interest. The similarity in general shape of all the curves is perhaps the most interesting feature. The curves become nearly linear at the higher pressures. This of course is not the usual relation between stress and work for a body like a steel spring, which maintains a stiffness independent of stress. For such bodies the work stored up as potential energy of strain varies as the square of the stress. This is true for liquids also over a pressure range so small that the compressibility may be regarded as constant, and is shown in the initial stages by all the curves, which are tangent to the axis at the origin. The fact that at high pressures the curves tend to become linear, still remaining slightly concave upwards, means that at high pressures the compressibility is becoming less, so that the change of volume, and therefore the work, is less for a given increment of pressure.

If we assume tentatively that the work of compression is linear at high pressures, we have a means of finding the compressibility and the volume at high pressures. For;

$$W = - \int_1^p p \left(\frac{\partial v}{\partial p} \right) dp = a + bp \quad (a \text{ is negative, } b \text{ positive}).$$

Differentiating this equation, we obtain,

$$\left(\frac{\partial v}{\partial p} \right)_t = - \frac{b}{p}$$

whence,

$$\Delta V = \int^p \left(\frac{\partial v}{\partial p}\right)_t dp = -b \, log \, p + C.$$

This equation cannot be expected to hold for low pressures. The constants may be determined as follows. From the curves for W above 5000 kgm. we find that an approximate value for b is 0.1. If furthermore we assume as a fair average of all twelve liquids that $\Delta V = -0.25$ when $p = 5000$, the equation becomes,

$$\Delta V = -0.1 \, log_e p + 0.6017.$$

The equation evidently cannot hold for infinite pressures, because it demands that ΔV decrease indefinitely, and it is physically impossible that ΔV should become less than -1.   But the pressure at which this would happen according to the above formula is 9,060,000 kgm.   This is so very far beyond the range of these experiments, that it would probably be safe to apply a similar equation as an approximate expression for any experimental pressures above 5000 kgm.

The mathematical analysis gives us, furthermore, information as to the ultimate behavior of the work of compression.   For the actual work must eventually be less than that given by the above formula, which corresponds to a smaller change of volume.   It must be, therefore, that at higher pressures the curvature reverses, and the curve becomes convex upwards.   Methyl and amyl alcohol show the beginning of this effect, but in view of the extreme remoteness of the vanishing of the volume predicted above, it may well be that this slight change of curvature is merely one of the many local variations.

The maximum amount of work stored up at 12000 kgm. is nearly the same for all twelve liquids; much more nearly equal than the initial differences in the compressibilities would lead us to expect. The variations in the maximum are about 25%, whereas there are initial variations in the compressibility of 100%.   If we admit water to our family of curves, as we may because the final work of compression is over 9 kgm. m., the variation in the initial compressibility may be 400%.   Initial differences of compressibility have little effect on the work at the maximum pressure, because of the comparatively small amount of work done at low pressures.

The total amount of mechanical work stored up in a liquid is quite considerable.   For example the work of compression of ether at 12000 kgm. would suffice to raise it through about 45000 ft., or to give it a velocity of 1700 ft. sec.

Heat of Compression.— The heat of compression, that is the quantity of heat in kgm. m. which flows out of a substance as it is compressed isothermally, is shown in Folder 4; for the twelve liquids separately in Figures 60 to 71, and the average for the twelve liquids collected into a single diagram in Figure 72. The differences of the curves for different temperatures are sufficiently great so that the total heat of compression for each temperature could be plotted and the difference found with sufficient accuracy directly from the curves, without the necessity of drawing difference curves as was the case for the work of compression. The zero of each curve has been displaced upwards one square for the successive temperatures. In the case of those liquids which boil at low temperatures, the zero of the curves for all temperatures has been taken at the same pressure, 500 or 1000 kgm., although it would have been possible to extend the curves to atmospheric pressure for the lower temperatures. In the case of acetone and ethyl chloride the curves for the lower temperatures have been extended backwards from the origin (1000 kgm.) to atmospheric pressure.

The heat of compression is positive, that is, as a substance is compressed isothermally, heat flows out to the surroundings. Examination of the curves in detail shows also that the total heat always increases with increasing pressure. This is a direct consequence of the fact that the thermal expansion is always positive. The curves therefore, show less pronounced irregularities than some, such as those for compressibility for example.

In general, the concavity is toward the pressure axis, that is, the increase of the heat of compression becomes less rapid at the higher pressures. The curves for the different liquids at different temperatures show that the heat is not universally greater at the higher temperatures, although such is generally the case. This is shown by the curves drawing together at high pressures in some cases to within less than the one square which separated them at the origin. An example of this is afforded by amyl alcohol between 20° and 40°, and by ethyl chloride and ethyl iodide between 60° and 80°. In general, a drawing together of the curves with increasing pressure means that the expansion is less at the higher temperature. There are many instances of this, although it is not usual that the drawing together is great enough to bring the curves to within less than the original arbitrary distance of separation.

Figure 72, in which are collected the average results for all twelve liquids, shows again that the twelve liquids are alike in character.

It is true that the curves cross in one or two instances, and are un-evenly spaced at the high pressures, but the differences are very much

TABLE XX.

COMPARISON OF THERMAL EXPANSION WITH HEAT OF COMPRESSION.

Liquid.	Expansion.		Heat of Compression	
	Expansion at Atmospheric Pressure.	Ratio to Average.	Heat at 12000 kgm.	Ratio to Average.
1	.00128	.91	18.0	1.04
2	120	.85	16.4	.95
3	115	.82	18.0	1.04
4	114	.81	16.0	.92
5	106	.75	14.9	.86
6	170(?)	1.20	17.4	1.01
7	172(?)	1.22	19.6	1.13
8	143	1.01	18.0	1.04
9	134	.95	17.5	1.01
10	190(?)	1.35	18.5	1.07
11	185(?)	1.31	18.3	1.06
12	120	.85	15.5	.89
Average	141		17.3	

Maximum variation of initial expansion, 1:1.8
Maximum variation of heat at 12000 kgm. 1:1.3

less than one would expect from the differences in the initial direction of the curves. The heat of compression is given by $Q = \int \tau \left(\frac{\partial v}{\partial \tau}\right)_p dp$, so that the relative initial values of $\left(\frac{\partial v}{\partial \tau}\right)_p$, that is the initial slopes

of the curves for Q, give us an idea of what we might expect to be the relative values of Q if the liquids preserved over the entire pressure range their relative initial behavior. Table XX shows this. It gives the initial dilatation and its ratio to the average, the total heat given out at 12000 kgm. and its ratio to the average. The dilatation tabulated for the low boiling liquids was obtained by a linear extrapolation, which gives values too small. Larger values for these liquids would only increase the force of the argument. It is obvious that the two ratio columns show only a general rough agreement; large values of one corresponding to large values of the other. There seems to be no correspondence in the small variations in the ratio column. This shows that the initial behavior of a liquid with respect to the heat of compression does not fix its behavior at the higher pressures. Furthermore, the magnitude of the variations in the ratios of the dilatation are greater than the variations of the heat ratios; a maximum variation in the one column of 1:1.8 against 1:1.3 in the other. This shows again that the liquids become more alike at the high pressures than we should expect from their initial behavior at atmospheric pressure.

The magnitude of the heat of compression is of interest. For the average liquid this is about 17 kgm. m. at 12000 kgm. If we take as a fair average for C_p 25 kgm. cm. this means that the amount of heat flowing out of the average liquid as it is compressed isothermally to 12000 kgm. would raise it through 68° at atmospheric pressure.

Change of Internal Energy. — This quantity is shown on Folder V; for the twelve liquids separately at four temperatures in Figures 73 to 84, and the average results for the twelve liquids plotted against pressure in Figure 85 and against volume in Figure 86. The change of energy plotted in these figures is the internal energy at atmospheric pressure minus the internal energy at the pressure in question. A positive value for the change means, therefore, that the internal energy is less at the higher pressure than it is at atmospheric. The origins of the curves for the separate temperatures have been displaced with respect to each other, so as not to confuse by over lapping. In the cases where the liquid boils at low temperatures the origin of the curve for the higher temperatures has been taken at 500 or 1000 kgm.

The change of internal energy was found by taking the difference between the heat and the work of compression. The curves show nothing, therefore, not already given.

The different substances show irregularities which cannot be dwelt

on here.   In general, the curves for the higher temperatures tend to draw apart, that is, the decrease of internal energy is greater at the higher temperature, but there are several well pronounced exceptions to this rule.   Amyl alcohol, ethyl chloride, and ethyl iodide, for example, are exceptional at the same temperatures where we found exceptional behavior with respect to the work of compression.

The change of internal energy is to be thought of as brought about by the counterplay of two opposing sets of forces, and it is significant because of what it can tell us about these forces.   When a substance is compressed, the molecules are brought closer together, the attractive forces between the molecules do work, the potential energy of the attractive forces decreases, and the internal energy decreases. But at the same time, the molecules become compressed by mutual contact, energy is stored up inside the molecule by the external forces in the form of potential energy of strain, and the internal energy increases.   Now these two sets of forces play very different roles at different stages of the compression.   At low pressures, where the molecules may be thought of as possessing a free path, no potential energy of strain can be permanently stored up in the molecule, because during the motion in the free path it has been entirely converted into translational kinetic or temperature energy.   This is what takes place in a gas.   But as the volume of the liquid becomes less, the length of the free path rapidly becomes smaller, and at any instant an increasingly large number of molecules is not describing part of any free path at all, but is merely being handed on directly from one collision to the next.   At this stage, potential energy of strain can be permanently stored up within the molecule.   At still higher compressions, when the molecules are practically in continuous contact, there is still greater possibility of storing up internal energy of strain.   The possibility is limitless, provided only that the molecule never becomes incapable of further compression.   The loss of internal potential energy by the attractive forces cannot proceed beyond a certain limit, however, imposed by the least distance of approach of the molecules.

We should expect, therefore, that at low pressures the internal energy would decrease with rising pressure, the attractive forces being in the ascendant, but at the higher pressures, where the forces resisting compression have become dominant, that the energy would increase with rising pressure.   For the two liquids previously investigated in this respect, mercury and water, the energy was found to continue to decrease over a pressure range of 12000 kgm.   The direc-

tion of curvature was in each case such as to suggest that this decrease might not continue indefinitely, and it was suggested then that there must ultimately be a reversal of the effect. It seemed surprising that at pressures as high as 12000 kgm. the attractive forces should still do more work than could be stored up as strain by the external forces.

Figure 85, giving the average for the twelve liquids, shows that the anticipation of a reversal in the change of energy is justified for nearly all the liquids; that is, the internal energy, after decreasing for a while, passes through a minimum (on the curves a maximum) and from here increases with rising pressure. The necessary existence of this maximum could of course have been predicted from the curves for the heat and the work of compression, since the one is either linear or concave upwards, while the other is concave downwards.

The change of energy is markedly different for the different liquids, whereas the other thermodynamic properties are similar. Of course the reason is that we are here concerned with the difference of two effects. The position of the maximum of the difference of two functions is very sensitive to slight changes in the functions themselves. Under these circumstances, the mere existence of a maximum is evidence of similarity. The only curves which do not show the maximum are methyl and propyl alcohol. It will be remembered that the work of compression curve for methyl alcohol had a reversed curvature at the upper end, and that the work of compression of propyl alcohol was abnormally low.

It is of interest to plot the change of energy against volume, because it may give information about the attractive forces. If the attractive forces are central forces, functions only of the distance from the centers of the molecules, then the potential energy of the attractive forces will be a function of the volume. Thus if the attractive forces are proportional to the inverse fifth power, as has often been supposed, then the potential energy is inversely as the fourth power of the distance apart of the molecules, or as the inverse four thirds power of the volume. This relation was tried for four of the twelve liquids; for amyl alcohol, ether, phosphorus trichloride, and ethyl iodide. The change of internal energy of these liquids was plotted against $V^{-\frac{4}{3}}$. The diagram was the same in character as the diagram plotting the change of energy against V, except of course that small values of $V^{-\frac{4}{3}}$ correspond to large values of V. Now if the change of internal energy is proportional to $V_0^{-\frac{4}{3}} - V^{-\frac{4}{3}}$, this curve plotted against $V^{-\frac{4}{3}}$ should be linear. The curves were very nearly linear in the in-

itial stages, but of course ultimately diverged greatly from linearity, passing through a maximum. If the straight portion of the curve at the origin represents a region in which the inverse four thirds power law is satisfied, then the tangent to the curve at the origin represents over the entire range of the experiment what the change of energy would have been if the four thirds law had held throughout. The difference between the actual curve and the tangent at the origin is then, according to the above view, equal to the energy which has been stored up as strain inside the molecule. This difference was determined and plotted against volume, in order to find what function of the volume the strain energy might be. For these four liquids, it turned out that the strain energy varies over the entire range approximately as the cube of the change of volume reckoned from a suitable origin. The greatest discrepancy is for ether at low pressures. For PCl_3 a variation of only 0.01 in the arbitrary zero of volume from which the change is reckoned would wipe out the discrepancy; for amyl alcohol a variation in the zero of 0.005 would give perfect agreement; for ethyl iodide a change of 0.01, and for ether a change of 0.04. The variation for ether is all below 3000 kgm.; above this the energy of strain is almost exactly proportional to the cube of the change of volume, taking 1.06 as the origin. The zero of volume for phosphorus trichloride is 1.11, for amyl alcohol 1.07, and for ethyl iodide 1.045. All the curves showed slight consistent variations from the cube law; at low pressures the strain energy varies more rapidly than the cube and less rapidly at the high pressures.

The fact that the internal energy of strain varies as the cube of the change of volume probably does not have very much significance in showing us what the elastic mechanism of the molecule is. If the entire change of volume of the liquid were due to change of volume of the molecules, then we should expect the strain energy to vary as the square of the change of volume, provided the elastic constants of the molecule were unaffected by pressure. If, as is likely, the molecule becomes less compressible at high pressure, then the strain energy would vary less rapidly than the square. But the strain energy was found to vary as the cube. The reason for this is probably that at low pressures strain energy is stored up in only a few of the molecules; those molecules which are describing a free path and are not in contact with other molecules have no strain energy of compression. With increasing pressure the number of molecules in which strain energy is stored up increases rapidly, and the strain energy of each molecule increases at the same time as the square of the strain,

so that the total energy of strain would be expected to increase more rapidly than the square of the change of volume, as we found it to. But any more detailed speculation as to the precise way in which the number of molecules taking part in the strain, and the way in which the strain energy of the average molecule varies with the total pressure, would probably be useless because the argument as to the attractive forces breaks down at small volumes. It is probable that the molecules are not really homogeneous spheres, but that there are localities in which the attractive forces are more or less concentrated. Therefore, although we may regard the attraction exerted by the molecule as toward its center, and inversely as the fifth power of the distance when the molecules are separated by wide intervals, we cannot conceive of this law continuing to hold when the molecules are so close as to be in contact. Under these circumstances the force may increase more rapidly than as the inverse fifth power. What is more, the potential energy of the attractive forces will not under these circumstances be a function of the volume only, that is of the mean distance apart of the centers of the molecules, but will also vary with the orientation. We saw that the average orderliness of orientation may be expected to vary with temperature, being on the whole more haphazard for equal volumes at the high temperatures. Even with this picture of what is happening, it would be difficult to say whether the potential energy of attraction should be expected to be greater at the higher or lower temperature. We have seen that the lower temperature usually means a greater space open for occupation, but it may still be that because of the greater approach to order at the low temperatures the localities of intense force are brought closer together, so that the potential of the attractive forces may be less.

The main conclusion to be drawn from the fact that the strain energy of the molecules varies as the cube of the change of volume is, therefore, that at low pressures the greater part of the change of volume is due to the decrease in the distance apart of the molecules, but that at high pressures an increasingly large part of the change of volume is occasioned by the actual change of volume of the molecules themselves.

It is interesting that the initial slopes of the curves of change of energy against volume are very nearly the same for all twelve liquids. This is a little unusual. Previously we have found the twelve liquids to become similar at high pressure, but in respect to the change of energy they appear to be more alike at low pressures.

Specific Heat at Constant Pressure.—The specific heat at constant pressure is shown on Folder VI; the curves for the twelve liquids at four temperatures in Figures 87 to 98, and the collection of the average results in Figure 99. The quantity listed as change of C_p is the specific heat at atmospheric pressure minus the specific heat at the pressure in question. A positive change means, therefore, that the specific heat is less at the pressure in question than at atmospheric pressure. In order not to confuse the curves, the origin for each temperature has been displaced with respect to the neighboring curves. The scale of the drawing is shown at the right hand side.

The twelve liquids show a bewildering variety, so bewildering that speculation as to the cause of all the variations is hopeless. It is to be pointed out nevertheless, that such great variety is to be expected if the molecules take up different positions more or less symmetrical in arrangement with increasing pressure. The process is similar in many ways to a process of association, which is accompanied by much greater changes in the specific heats than in the volume, or compressibility, or dilatation. The curves show some points of similarity, however. It is an almost universal rule that the initial change of C_p at any temperature is a decrease. For the majority of liquids the specific heat on the whole decreases at the high temperature and increases or does not increase so much at the low temperatures. We have seen that as a rule the specific heat at atmospheric pressure is higher at the higher temperatures. For some liquids the temperature effect may be very marked. The change under pressure is in such a direction as to bring the specific heats at high pressures more nearly to equality for all the temperatures. The three halogen compounds are an exception to the rule, however. The very large increase of C_p for ethyl chloride at 80° is very much like that already found in the case of water. It may mean an abnormally high rate of dissociation at the higher pressures. The four normal alcohols show similarities in the abnormally large decrease of C_p at 80°. The decrease evidently cannot go on indefinitely. For methyl and ethyl alcohol, the maximum pressure is sufficient to change the decrease into an increase, as it must eventually, but for propyl and amyl alcohols, the reversal in direction must be at higher pressures than reached here. It seems to be at hand for propyl alcohol.

There is one very rough check which may be applied to the values given here for the specific heats; namely, in no case must the specific heat decrease by an amount more than its original value, for a nega-

tive specific heat is impossible. The only case where this condition comes anywhere near making trouble is for amyl alcohol. The curve for 80° shows a decrease of C_p of 21 kgm. cm.   The data for atmospheric pressure are discordant, but 25 kgm. cm. seems to be a fair average value at 80°. This would mean that the specific heat at 80° and 12000 kgm. is only 4 kgm. cm., about one sixth its initial value. It is evident that the reversal in the effect must come speedily.

Figure 99 for the average change of C_p over the entire temperature range for the twelve liquids shows much less variation from liquid to liquid than one might expect from the irregular variations at the different temperatures. The curves in general all show the same characteristics; at first a decrease of specific heat and then an increase at higher pressures. The first minimum has already been commented on in another connection.   Beyond this minimum in C_p (maximum on the curves) there is in general a continuous increase with rising pressure, although there are several cases where C_p decreases again slightly at the highest pressures. The three halogen compounds are exceptional (and also acetone) for the rather large increase of C_p with rising pressure. The increase is greater for the heavier members of the series.

The data of the previous paper on water show the same behavior, a minimum in C_p for all temperatures (except at 0° where the curve is broken off by the freezing) and then an increase with still further increasing pressure. The pressure for the minimum is higher than for these twelve liquids because of the abnormal behavior of water at low pressures.

So far as is known to the author, these are the only measurements from which an attempt has been made to find the specific heat at high pressures. The probable behavior of the specific heats does not seem to have been suspected. Thus Tumlirz deduces from his empirical equation for liquids that both the specific heats decrease with rising pressure. For water, Tumlirz finds the limiting value of C_p for infinite pressure to be about 0.5 gm. cal. He does not compute it for the other liquids. We see from the above that we are to expect for all liquids an ultimate increase instead of a decrease with rising pressure.

Specific Heat at Constant Volume. — The specific heat at constant volume is shown in Folder VII, the curves of the different liquids at different temperatures in Figures 100 to 111, and the collected averages for all the liquids in Figure 112. The treatment of these curves is the same as for C_p.

The curves are the same in general character as those for C_p. The differences consist in displacements of the pressures of maximum or mimimum, or occasionally in the suppression of small irregularities; but the larger features are the same.   The curves for the four normal alcohols retain the same resemblances as before, and isobutyl alcohol is as strikingly not a member of the series.   Isobutyl alcohol and ether show general resemblances as to the specific heat, which may, however, be accidental.   The halogens are also different from the other liquids with respect to C_v.

The importance of tabulating C_v is that it is a quantity of much greater simplicity than C_p.   When we determine C_p by heating the liquid at constant pressure, the liquid expands with rising temperature, and in so doing performs work against both the external pressure and the internal attractive forces. C_p is greater than C_v by this work against external and internal forces. Consequently, it is usual to tacitly assume that C_v contains only the work necessary to raise the temperature energy of the molecules.   Evidently the assumption is merely another way of stating the assumption that the potential energy of the attractive forces is a function of the volume only. Furthermore, it is usually assumed in discussions of the significance of C_v that a given increase of temperature corresponds to a given increase of kinetic energy of the molecule, no matter what the pressure of the liquid.   It is true that when the kinetic energy of the molecule is to be raised, more total energy must be imparted to the molecule than just sufficient to increase the kinetic energy by this amount, because of the law of the equipartition of energy among the various degrees of freedom, but if the degrees of freedom remain unaltered, we still have the result that to increase the temperature by a given amount requires the same amount of work independent of the volume. The consequence of the hypothesis would be that the specific heat at constant volume is independent of pressure and temperature.

Figure 112 for the average C_v of the twelve liquids, shows that even on the average C_v cannot be independent of pressure, and the preceding diagrams for the separate liquid show that it certainly cannot be independent of temperature.   In general the behavior of C_v seems to be at first a decrease, and then with increasing pressure an increase again.   Probably the reason is that neither of the simple hypotheses which we discussed above are valid for high pressures.   We have seen that at high pressures we may expect the molecules to approach positions of more or less regularity of arrangement, and that the regularity is greater at the low temperatures.   Now according to the

particular arrangement which the molecules adopt, and the relation of the local centers of force to this arrangement, it is conceivable that the potential of the attractive forces should be either greater or less at the lower temperatures and equal volumes. The likelihood is, however, that the potential will usually be less at the lower temperatures. Similarly, it is usually more likely that the potential of the attractive forces should be less at the higher pressures. As a rule, then, an increase of temperature of one degree at a higher pressure or a lower temperature must provide the energy to do more work against the attractive forces, so that the specific heat at constant volume will be greater at higher pressure and lower temperature. But in those more infrequent cases where the potential energy of position is less at the higher temperature or lower pressure, the specific heat will be less at higher pressures and lower temperatures. It is as a rule true, as we have seen from the curves, that C_v does become greater at the higher pressures and lower temperatures.

The considerations just discussed are somewhat similar to considerations regarding the association of the molecules, but do not in all cases lead to the same results. For instance, if we suppose a liquid of single molecules to associate to one of double molecules, the specific heat of the associated liquid would be one half that of the simple one, if we neglect the effect of the altered number of internal degrees of freedom.

The second hypothesis made above, that a given increase of temperature always corresponds to the same increase of molecular energy, probably breaks down also at high pressures. The difficulty of determining what happens in this case is increased by uncertainty as to what the definition of temperature shall be at high pressures. We may perhaps, however, think of temperature at low pressures as being roughly proportional to the average translational energy of the molecule during its free flight. Now we have seen that as pressure increases, the time of free flight decreases rapidly, and an increasing fraction of the time is spent in collision. During collision the kinetic energy of translation has become potential within the molecule. The result is that as pressure increases, the potential strain energy of the molecules becomes a greater part of the total energy, leaving a smaller residue to become kinetic. Now if temperature corresponds to translational kinetic energy, it is evident that at high pressures more total energy must be imparted to the substance to increase the translational energy a given amount, or in other words, the specific heat will increase with increasing pressure.

The initial decrease of C_v may very possibly be an association effect. A word should be said about this association effect. The reason that an association from single to double molecules, for example, reduces the specific heat to one half, neglecting the effect of the internal degrees of freedom, is that a rise of temperature of one degree corresponds to a definite increase in the kinetic energy of each molecule, and when there are half as many molecules, half the additional energy is needed to increase the energy by an amount corresponding to one degree. This means that association has an effect on specific heat as long as temperature remains a molecular affair. This is true for a gas. But the law of atomic heats for solids suggests very strongly that in solids temperature is no longer an affair of the molecule, but has become a matter of the atom. We naturally expect somewhere a transition from the one state to the other, and the liquid is the natural place to look for it. That is, if a liquid temperature is on its way from being an affair of the molecule to becoming an affair of the atom. It is not likely, therefore, that the existence of large molecular complexes in a liquid, as in the case of association, will modify very much the behavior with respect to temperature, and in particular to the specific heats. Such effect as there is should be looked for at low pressures.

A word should be said about the curves for the average of C_p and C_v over the entire temperature range. The average C_p is the total heat absorbed at constant pressure between 20° and 80° divided by 60. C_v is the average of the four values at 20°, 40°, 60°, and 80°. These two averages are not always equivalent when there are large variations with temperature, but they are always approximately equal. In cases of question, the average C_p corresponding to C_v may be found from the curves for C_p at the four temperatures. To find the average C_v corresponding to the average C_p would involve a more complicated procedure.

GENERAL DISCUSSION OF THE BEARING OF THE RESULTS ON A THEORY OF LIQUIDS FOR HIGH PRESSURES.

It is proposed to discuss here the nature of the problems which confront one at high pressures. No attempt is to be made to develop a new theory, but merely to indicate some of the directions in which the data of this paper suggest modifications of conceptions which have hitherto worked at low pressures.

Perhaps the most far reaching modification is in regard to our

idea of the kinetic origin of pressure. We suppose that the pressure of a gas, for instance, is produced by the impact of the molecules against the walls of the vessel; and we compute the magnitude of the pressure from the total change in one second of the momentum of the molecules striking on unit area of the wall. The velocity with which the molecules strike the walls decreases with falling temperature and vanishes at the absolute zero. The pressure exerted by a liquid also is thought of in most attempts at a theory of liquids as exerted by the same mechanism and is computed in the same way. But it is entirely obvious that the molecules may exert pressure on the walls in another way. It is inconceivable that at the absolute zero a substance should not resist an attempt to compress it; yet at this temperature there can be no kinetic effect exerted by the molecules as a whole. Under these conditions the molecules transmit pressure in the same way that a compressed spring does; that is, they behave like elastic solids. It does not concern us here to inquire what the ultimate origin of this elasticity is; it may be kinetic within the atom. The point is simply this; from our point of view, which regards the molecule as a whole, we must recognize two possible functions or modes of action; the molecule may behave like a moving centre of mass with kinetic energy and momentum, or it may behave like an elastic solid. The molecule may exert pressure in virtue of either one of these two modes of action. Under ordinary conditions the momentum effect of its motion as a whole is almost the entire effect. But if we examine the mathematical analysis which justifies us in putting the pressure equal to the total change of momentum in unit time, we shall find that we made certain simplifying assumptions. We assumed that each collision with the wall is unimpeded; that is, the molecule approaches the wall during free flight, has a single encounter and makes a clean get-away. And this assumption was necessary; as soon as the molecule is interfered with during its collision, as it may be by a collision from another molecule from behind, the simple change of momentum relation ceases to give the pressure, and we must treat our molecule during collision as an elastic solid. Now it is evident that as the volume becomes less, that is, as the pressure increases, the total number of collisions with interference will increase, and our kinetic conception of pressure becomes less and less useful.

A very simple model, which may or may not correspond to the physical facts, is instructive in showing how under different conditions we may compute the pressure from the momentum effect alone, or must consider also the elasticity effects. The substance we are

to consider consists of a single molecule. The molecule consists of a heavy particle of mass m, with two weightless springs projecting on either side of length l_0, giving a total diameter of the molecule of $2l_0$. (Figure 113.) This molecule travels back and forth in a horizontal line between the two opposite vertical walls of the enclosure.
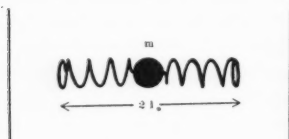
FIGURE 113. Model of a substance consisting of one molecule. The model is to show that at high compressions the pressure is not given by the change of momentum of the molecules striking the walls of the vessel in unit time.

The distance apart of the walls is the volume of the enclosure, the force exerted by the springs on the walls during an encounter gives the pressure exerted by the substance, and the kinetic energy of the particle at its maximum velocity represents temperature.

This model is so simple that the entire discussion may be carried through with rigorous mathematical analysis. The pressure exerted on the walls is evidently to be found by taking the time average (over a long interval of time) of the force exerted on the walls by the springs during the encounters. Now in the solution of this problem there are three different cases.

I. The first case is when the distance apart of the walls of the vessel is greater than $2l_0$, the diameter of the molecule. Under these conditions we have collision without interference, which are the only conditions to which the usual analysis applies. In this case it may be proved by a detailed mathematical solution which will not be given here that the time average of the force is exactly equal to the change of momentum in unit time with respect to one of the walls, as it should be. The results of the mathematical analysis for this case may be given in the form of a distinctive equation of the substance,

$$P\left[(v - b) + a\, T^{\frac{1}{2}}\right] = 2\, T.$$

Here P is pressure, v = volume (distance apart of walls), b = diameter of molecule ($2l_0$), $a = \pi\sqrt{\dfrac{2}{k}}$, where k is elasticity of the springs, and T = absolute temperature (kinetic energy of particle). The equation bears a resemblance to van der Waal's equation without the attractive forces. In van der Waal's equation $a = 0$, or $\kappa = \infty$, which means that the time of collision of the particles with the wall may be neglected in comparison with the time of free flight.

II. The distance apart of the walls is less than $2l_0$, the diameter of

the molecule, and the kinetic energy of agitation is so small that at no time is the molecule out of contact with *both* walls simultaneously. The detailed mathematical solution shows that under these conditions the momentum effect has no influence whatever, and the pressure is determined simply by the relative magnitude of the volume and the unstressed diameter of the molecule.   Under these conditions we obtain as the characteristic equation

$$P = \frac{k}{2} (b-v).$$

It is remarkable that the temperature has disappeared from the characteristic equation, or, in other words, the thermal dilatation is zero. The substance still remains compressible, however. Something like this was expected for the liquids of these experiments; that is, it was expected that the dilatation would tend to vanish more rapidly then the compressibility.

III. Case II passes into this case when the violence of the temperature vibration becomes so great that during part of the vibration the molecule is in contact with only one wall. The critical temperature at which this occurs is when $T = k \left(\frac{b-v}{2}\right)^2$. The mathematical analysis is more complicated for this case, because the motion must be split up into two stages, during which the restoring forces are different functions of the displacement. But just as in Case II, the change of momentum of the molecule in unit time does not give the mean pressure exerted on the wall. The complete equation of state for Case III is complicated, involving antisines, so that it is hardly worth giving. It reduces to one or the other of the other two cases, however, under proper critical conditions. In this case, the pressure computed by the change of momentum is too low, as we should expect it would be, because we have neglected an elasticity term which modifies conditions when the molecule is in contact with both walls.

The sequence of events when we compress a substance at a given temperature from a large volume is first Case I, then Case III, when $v = b$, and then Case II, when the volume has been still further reduced by an amount depending on the temperature. Case I passes smoothly into Case III without discontinuity in either compressibility or dilatation. The difference between Cases I and III is that a higher pressure corresponds to a given volume in Case III than we should expect from the formula of Case I. The pressure at a given volume in Cases I and III depends on temperature, but in Case II, the rela-

tion between volume and pressure is the same for every temperature. The only way in which temperature has an effect in Case II is with regard to the critical temperature which determines when Case II passes into Case III. The pressure for a given volume in Case III ultimately becomes less than we would have expected it to be if we extrapolated by the formula of Case I. In other words, the substance is more compressible than we should expect it to be from its behavior at low pressures. This reminds us of the formulas of Tumlirz and Tammann. It should be said however, that the mathematical analysis applied to Case III cannot continue to have physical significance indefinitely, for it was assumed that the springs obey Hooke's law, which is true only for small displacements. The characteristic equation given above for Case III predicts the vanishing of the volume at a finite pressure.

Something similar to the action of the model must take place in a liquid. At any instant there are collisions taking place, some free collisions similar to those of Case I, some collisions with interference like Case III, and some contacts between molecules like Case II, which are not properly called collisions at all. The momentum computation of pressure applies only to Case I. At low pressures, by far the greater number of collisions is of type I, but as the volume decreases and pressure increases, collisions of type II and III become increasingly predominant, until at infinite pressure we may suppose type II only to be present. Under these conditions, the momentum effect has absolutely no connection with pressure.

The ordinary conception of internal pressure must obviously be modified in a similar way. There are many different meanings attached to "internal pressure." One way of defining internal pressure is by constructing an imaginary surface in the interior of a liquid, and finding the momentum of all the molecules which cross this surface in unit time. This process evidently fails to have physical meaning when there are molecules in the liquid in contact with each other for any length of time. The modification of the definition necessary to meet these new conditions would be very complicated. It seems better under the circumstances to give up this conception of internal pressure altogether. Other conceptions may still be useful at high pressures; such, for example, as to regard the internal pressure as the external pressure plus the unbalanced attractive effect of the molecules at the surface of the liquid. But it is a difficult matter to define internal pressure in such a way as to have a physical meaning for one of Maxwell's demons inhabiting the interior of a liquid.

Accordingly, in the previous discussion no use has been made of this "internal pressure."

The usual kinetic conception of temperature must undergo modification at high pressures just as our kinetic conceptions of pressure. We think of the temperature of a gas as proportional to the average kinetic energy of translation of its molecules, the translational energy being the energy of the center of mass during free flight. Now it is inconceivable that at infinite pressure there should be any free flight, that is, there can be no kinetic energy of the molecule as a whole, but it is also inconceivable that at infinite pressures a substance should not possess temperature and be capable of temperature equilibrium with surrounding objects. Our model of the molecule may be helpful to us again. When the volume decreases beyond a certain limit, we saw that the boundaries of the molecule become fixed in position, and that the temperature is represented by the energy of internal agitation. This suggests that temperature changes in character from an affair of the molecule as a whole at low pressures to an affair of agitation within the molecule at high pressures. The behavior of the specific heats of gases and solids also strongly suggests the same thing. We compute the specific heat at constant volume of a gas by supposing that the kinetic energy of translation of each molecule must be increased by a fixed amount to produce a rise of temperature of one degree. But for most solid elements the law of Dulong and Petit holds, which is equivalent to the statement that to increase the temperature of a solid by one degree we must increase the energy of each atom by a fixed amount. Now a microscopic analysis of a solid like iron discloses a crystalline structure of great complexity; we find it hard to think that there are not groups of associated molecules and that the molecules are monatomic. It appears, then, that temperature has become connected somehow with what is going on in the atom. It view of this it would seem that another conception of temperature is desirable. It must be such a conception as not to be at variance with what we suppose to happen in a gas or a solid.

The material for such a conception is at land. It is a property common to the temperature energy of a gas molecule and to the internal energy of our suppositious molecule, that it is constantly in a state of flux, changing during collision from kinetic to potential and back to kinetic again. A natural generalization, then, is as follows: Temperature is proportional to that part of the energy associ-

ated with a representative molecule which undergoes periodic changes from kinetic to potential and back to kinetic. In complicated cases where the transformation from kinetic to potential does not take place simultaneously in all parts of the atom, an equivalent generalization is: Temperature is the difference between the maximum and minimum potential energy of a representative molecule. This evidently applies to both the extreme cases above; the one for which temperature is proportional to kinetic translational energy, and the one for which it is proportional to internal energy. In one respect these two extreme cases are not entirely unlike; in accordance with the law of equipartition, only a certain proportion of the total energy communicated to a molecule of a gas becomes kinetic; the rest goes to the internal degrees of freedom. So that an increase of temperature always carried with it an increase of the internal energy of the molecule. Whether this internal energy also oscillates in character between kinetic and potential is not obvious.

Of course the justification of this proposed general definition of temperature must be furnished by experiment. It does have the advantage, however, of being applicable at high pressures where the ordinary definition breaks down completely, and it does agree with our physical feeling of what temperature must be in the case of one very simple model of a substance under high pressure.

The effect of this conception of temperature on our conception of the equipartition of energy between the different degrees of freedom is interesting. At high pressures, where the molecules press on each other from all sides, one degree of freedom has been lost (or more properly three) namely, the possibility of motion of the molecule as a whole. We may suppose, if we like, that under these circumstances the total energy is equally divided between the remaining degrees of freedom. Now at any instant in a liquid, there are molecules with varying degrees of freedom, according to the kind of collision in which they are entangled. Furthermore, the same molecule at different stages of its career may enjoy a different number of degrees of freedom. When the degrees of freedom change, there must follow a redistribution of the total energy among the remaining degrees of freedom, and this process takes time. The result is that we cannot ascribe to the average molecule of the substance any definite number of degrees of freedom. The number cannot be an integer in the first place, and in the second place must vary continuously as pressure varies.

The idea that the temperature of a substance need not be propor-

tional to the kinetic energy of translation of the molecules is not new. For instance, there is a recent paper by Brillouin,[59] in which he discusses at length the possible necessity of a change in the usual defininition of temperature as the volume changes.

One other very important consideration which we shall probably be obliged to introduce into a theory valid for high pressures has already been mentioned several times in the discussion of the various thermodynamic properties. It is this; in gases we think of the molecules as perfect spheres, but at high pressures we shall undoubtedly have to recognize that they possess more complicated shapes. It is inconceivable that a molecule should not have a characteristic shape; we cannot well imagine the possibility of so fitting together the atoms of a complicated organic compound as not to produce some irregularities in the molecule. Shape becomes increasingly important at high pressures where the molecules are forced together and constrained to adapt themselves as best they can to each others irregularities. Beside the possibility of shape, there is the possibility that there are local centers of force in the molecule; that we cannot regard the molecule as a homogeneous sphere exerting a force towards its own center, but that when we approach too close to the molecule, there are individualized centers of force that begin to act of their own account. This again, seems by no means a forced conception.

Along with the idea of molecules with shape goes the conception that at high pressures these shapes must be forced to more or less adapt themselves to each other; in other words, the molecules must begin to show traces of regular arrangement. The regularity is by no means the thorough going regularity of a crystal in which the molecules are permanently moored to certain mean positions: the molecules of the liquid still circulate about among each other, but as they slide past each other there may be a growing tendency at higher pressures to point the long axes in the direction of relative motion, for example. Just as at a crowded ball room, there is a tendency for the throng of young men making their way to and from the refreshment room to hold their plates out from them in the direction of motion. This increasing order of arrangement seems not only natural, but inevitable at high pressures. It may ultimately terminate in crystallization. We should expect furthermore, at equal volumes, there should be nearer approach to order at lower temperatures where the violence of temperature agitation is less.

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[59] Brillouin, Ann. Chim. et phys., **18**, 387–400 (1909).

Now the combination of these two effects, namely that when the molecules come very close to each other the attractive forces depend on the orientation as well as on the mean distance apart, and that the molecules may assume a greater uniformity of arrangement, has far reaching consequences that provide the possible explanation of all the complicated effects which we have found to exist. Thus, if we consider two possible configurations of the liquid, each having the same volume, but one with a more orderly arrangement of the molecules, we see that the more orderly arrangement involves a greater effective space open to occupation. One consequence is that the more orderly arrangement has the greater compressibility. One striking example of this has been found in the case of mercury. The compressibility of solid mercury has been found to be less than the compressibility which the liquid would have at the same temperature if it could be compressed without freezing to the same volume as the solid.

In the detailed discussion of the thermodynamic properties it has been shown that we have here a possible explanation of many complicated effects. It explains increasing compressibility with rising pressure, decreasing compressibility with rising temperature, increasing thermal expansion with increasing pressure, and decreasing expansion with rising temperature. It is not necessary to go into the details of the argument again. It is to be emphasized, however, that we have here a mechanism capable of explaining a bewildering array of experimental facts. There must be at least some validity in the point of view.

Not much has been said in the explanation above of the results of possible association, because under high pressures, when the molecules find difficulty in adapting themselves to the space at their disposal, it seems unlikely for groups of molecules to unite themselves into very close knit units. The molecules, on the other hand, do apparently preserve their individuality under these high pressures, and do not break up into simpler compounds. It might be expected, for instance, that pressure would transform ether into isobutyl alcohol, a substance of the same atomic constitution, but with a smaller volume. Such was not the case, however. But it may be that association does play an important part at low pressures. In this case it would be capable of explaining various irregularities in very much the same way as suggested above. For instance, if association takes place with decrease of volume, the thermal expansion or compressibility may be

greater at lower than at high temperatures. Association has been discussed in greater detail on page 104.

The results have exhibited one striking feature which has been frequently emphasized, namely that at high pressures all twelve liquids become more nearly like each other. This suggests that it might be useful in developing a theory of liquids to arbitrarily construct a "perfect liquid" and to discuss its properties. Certainly the conception of a "perfect gas" has been of great service in the kinetic theory of gases; and the reason is that all actual gases approximate closely to the "perfect gas." In the same way, at high pressures all liquids approximate to one and the same thing, which may be called by analogy the "perfect liquid." It seems to offer at least a promising line of attack to discuss the properties of this "perfect liquid," and then to invent the simplest possible mechanism to explain them.

SUMMARY OF RESULTS.

These measurements have disclosed an unexpectedly complicated state of affairs at high pressures, in many respects the exact opposite of what we would expect from the behavior at low pressures. The compressibility may decrease with increasing temperature, or in a few cases may increase with increasing pressure. The thermal expansion also may decrease with increasing temperature or increase with increasing pressure. The peculiarity of thermal expansion with respect to temperature is possessed by all liquids above 3000 kgm. This has been shown to have a bearing on previous theories. Of the other thermodynamic properties, perhaps the most important is the internal energy. This passes through a minimum and then increases again with increasing pressure. The reason is that beyond a certain pressure the attractive forces do less work than is done by the external forces in compressing the molecule.

Among considerations which would seem to be of importance for a theory of liquids at high pressures, that of the shape of the molecules is worthy of attention. It is inconceivable that the molecules should not have shape, and it is natural to suppose that the shape will play an important part when the molecules are forced into close contact. It is shown in detail that considerations of this sort offer possible explanations of the complicated effects actually found. Other modifications of the ordinary conceptions of liquids that may be necessary have to do with our ideas of the kinetic origin of pres-

sure and temperature.   There can be no doubt that at high pressures
there are other than kinetic effects involved at least in pressure.

It is a pleasure to acknowledge generous assistance from the Rumford Fund of the American Academy of Arts and Sciences for the purchase of apparatus and supplies, and from the Bache Fund of the National Academy for an assistant in some of the experimental work.

Thermal Dilatation

Pressure, kgm. / cm.² x 10⁻³

Methyl Alcohol

FIGURE 20.

Thermal Dilatation

Pressure, kgm. / cm.² x 10⁻³

Ether

FIGURE 25.

Thermal Dilatation

Pressure, kgm. / cm.² x 10⁻³

Ethyl Alcohol

FIGURE 21.

Thermal Dilatation

Pressure, kgm. / cm.² x 10⁻³

Acetone

FIGURE 26.

Thermal Dilatation

Pressure, kgm. / cm.³ x 10⁻³

Propyl Alcohol

FIGURE 22.

Ethyl Chloride

FIGURE 29.

Ethyl Bromide

FIGURE 30.

Ethyl Iodide

Methyl Alcohol

FIGURE 20.

Thermal Dilatation

.0010

.0006

.0002

0 1 2 3 4 5 6 7 8 9 10 11 12
Pressure, kgm. / cm.² x 10⁻³
Ethyl Alcohol

FIGURE 21.

Thermal Dilatation

.0010

.0006

.0002

0 1 2 3 4 5 6 7 8 9 10 11 12
Pressure, kgm. / cm.² x 10⁻³
Propyl Alcohol

FIGURE 22.

Thermal Dilatation

.0014

.0010

.0006

.0002

0 1 2 3 4 5 6 7 8 9 10 11 12
Pressure, kgm. / cm.² x 10⁻³
Isobutyl Alcohol

FIGURE 23.

0 1 2 3 4 5 6 7 8 9 10
Pressure, kgm. / cm.² x 10⁻³
Ether

FIGURE 25.

Thermal Dilatation

.0018

.0014

.0010

.0006

.0002

0 1 2 3 4 5 6 7 8 9 10 11
Pressure, kgm. / cm.² x 10⁻³
Acetone

FIGURE 26.

Thermal Dilatation

.0014

.0010

.0006

.0002

0 1 2 3 4 5 6 7 8 9 10 11
Pressure, kgm. / cm.² x 10⁻³
Carbon Bisulphide

FIGURE 27.

Thermal Dilatation

.0010

.0006

Thermal Dilatation

.0014

.0010

.0006

.0002   0 1 2 3 4 5 6 7 8 9 10 11 12
Pressure, kgm. / cm.² x 10⁻³
Ethyl Chloride

FIGURE 29.

Thermal Dilatation

.0010

.0006

.0002

0 1 2 3 4 5 6 7 8 9 10 11 12
Pressure, kgm. / cm.² x 10⁻³
Ethyl Bromide

FIGURE 30.

Thermal Dilatation

.0014

.0010

.0006

.0002

0 1 2 3 4 5 6 7 8 9 10 11 12
Pressure, kgm. / cm.² x 10⁻³
Ethyl Iodide

FIGURE 31.

Thermal Dilatation

1
2
3
4
5
6
7
8
9
10

0.0010

Pressure, kgm. / cm.² x 10⁻³
Propyl Alcohol

FIGURE 22.

Pressure, kgm. / cm.² x 10⁻³
Isobutyl Alcohol

FIGURE 23.

Pressure, kgm. / cm.² x 10⁻³
Amyl Alcohol

FIGURE 24.

Pressure, kgm. / cm.² x 10⁻³
Carbon Bisulphide

FIGURE 27.

Pressure, kgm. / cm.² x 10⁻³
Phosphorus Trichloride

FIGURE 28.

Folder I. The thermal expansion, $\left(\frac{\partial v}{\partial \tau}\right)_p$, against pressure. In Figures 20 to 31 the thermal expansion for the separate liquids at 20°, 40°, 60°, and 80° is shown against pressure. In Figure 32 the average expansion between 20° and 80° is plotted against pressure for all twelve liquids in a single diagram. In the curves for the separate liquids, the curves cross and recross so many times that it would be confusing to try to determine from the diagrams alone what curve belongs to each temperature. The following detailed description is given, therefore, of the order of the curves at intervals of 2000 kgm., reading from below up.

FIGURE 20. Methyl Alcohol. The order of the curves, reading from below up, is as follows; at 1 kgm., 20°–40°–60°–80°; at 2000 kgm., 40°–60°–80°–20°; at 4000 kgm., 80°–60°–40°–20°; at 6000 kgm., 80°–60°–40°–20°; at 8000 kgm., 80°–60°–40°–20°; at 10000 kgm., 60°–40°–20°–80°; and at 12000 kgm., 80°–20°–40°–60°.

FIGURE 21. Ethyl Alcohol. The order of the curves, reading from below up, is as follows. At 1 kgm., 20°–40°–60°–80°; at 2000 kgm., 20°–40°–60°–80°; at 4000 kgm., 80°–60°–40°–20°; at 6000 kgm., 80°–60°–40°–20°; at 8000 kgm., 60°–80°–40°–20°; at 10000 kgm., 60°–40°–80°–20°; and at 12000 kgm., 20°–80°–40°–60°.

FIGURE 22. Propyl Alcohol. The order of the curves, reading from below up, is as follows; at 1 kgm., 20°–40°–60°–80°; at 2000 kgm., 20°–40°–60°–80°; at 4000 kgm., 80°–60°–40°–20°; at 6000 kgm., 80°–60°–40°–20°; at 8000 kgm., 80°–60°–40°–20°; at 10000 kgm., 40°–60°–20°–80°; and at 12000 kgm., 40°–20°–60°–80°.

FIGURE 23. Isobutyl Alcohol. The order of the curves, reading from below

up, is as follows. At 1 kgm., 20°–40°–60°–80°; at 2000 kgm., 60°– 80°; at 4000 kgm., 80°–20°–40°–60°; at 6000 kgm., 80°–60°–20°– 8000 kgm., 80°–60°–40°–20°; at 10000 kgm., 80°–60°–40°–20°; 12000 kgm., 80°–60°–40°–20°.

FIGURE 24. Amyl Alcohol. The order of the curves, reading from up, is as follows. At 1 kgm., 20°–40°–60°–80°; at 2000 kgm., 60°– 20°; at 4000 kgm., 60°–80°–40°–20°; at 6000 kgm., 60°–40°–80° 8000 kgm., 60°–40°–20°–80°; at 10000 kgm., 20°–40°–60°–80° 12000 kgm., 80°–20°–40°–60°.

FIGURE 25. Ether. The order of the curves, reading from is as follows. At 1 kgm., 20°; at 2000 kgm., 20°–40°–60°–80°; at 80°–60°–40°–20°; at 6000 kgm., 80°–60°–40°–20°; at 8000 kgm. 40°–20°; at 10000 kgm., 20°–40°–60°–80°; and at 12000 kgm., 20°– 60°.

FIGURE 26. Acetone. The order of the curves, reading from is as follows. At 1 kgm., 20°–40°–60°; at 2000 kgm., 80°–60°– at 4000 kgm., 60°–80°–40°–20°; at 6000 kgm., 80°–60°–20°–40° kgm., 80°–60°–20°–40°; at 10000 kgm., all equal; and at 12000 60°–40°.

FIGURE 27. Carbon Bisulphide. The order of the curves, re below up, is as follows. At 1 kgm., 20°–40°–60°–80°; at 2000 kgm 20°–80°; at 4000 kgm., 80°–20°–40°–60°; at 6000 kgm., 80°–20° at 8000 kgm., 80°–60°–40°–20°; at 10000 kgm., 80°–60°–40°–20 12000 kgm., 20°–80°–40°–60°.

FIGURE 28. Phosphorus Trichloride. The order of the curve from below up, is as follows. At 1 kgm., 20°–40°–60°–80°; at 2

Pressure, kgm. / cm.² x 10⁻³

Ethyl Iodide

FIGURE 31.

Pressure, kgm. / cm.² x 10⁻³

FIGURE 32.

20°– 40°– 80°– 60°; at 4000 kgm., 80°– 20°– 60°– 40°; at 6000 kgm., 80°– 20°– 40°– 60°; at 8000 kgm., all equal, at 10000 kgm., 80°– [20° and 60°]– 40°; and at 12000 kgm., 80°– [20° and 60°]– 40°.

FIGURE 29. Ethyl Chloride. The order of the curves, reading from below up, is as follows. At 1 kgm., 20°; at 2000 kgm., 80°– 20°– 40°– 60°; at 4000 kgm., 80°–[20° and 60°]–40°; at 6000 kgm., 80°– 60°– 40°– 20°; at 8000 kgm., 80°– 60°– 40°– 20°; at 10000 kgm., 60°– 40°– 80°– 20°; and at 12000 kgm., 80°– 20°– 40°– 60°.

FIGURE 30. Ethyl Bromide. The order of the curves, reading from below up, is as follows. At 1 kgm., 20°; at 2000 kgm., 80°– 60°– 40°– 20°; at 4000 kgm., 80°– 60°– 40°– 20°; at 6000 kgm., 80°– 60°– 40°– 20°; at 8000 kgm., 60°– 40°– 80°– 20°; at 10000 kgm., 80°– 60°– 40°– 20°; and at 12000 kgm., 80°– 20°– 40°– 60°.

FIGURE 31. Ethyl Iodide. The order of the curves, reading from below up, is as follows. At 1 kgm., 20°– 40°– 60°– 80°; at 2000 kgm., 80°– 60°– 40°– 20°; at 4000 kgm., 80°– 60°– 40°– 20°; at 6000 kgm., 80°– 60°– 40°– 20°; at 8000 kgm., 80°– 60°– 40°– 20°; at 10000 kgm., 60°– 80°– 40°– 20°; and at 12000 kgm., 80°– 20°– 60°– 40°.

FIGURE 32. The average dilatation between 20° and 80° for all twelve liquids. The numbers on the curves indicate the liquids in the same order as the diagrams for the separate liquids. In order to prevent overlapping the origin of each curve has been displaced one square with respect to the one next to it. The origin is so situated that the dilatation for all the liquids at 12000 kgm. is between 0.0002 and 0.0003. The scale is shown at the right hand side. As an example of the use of the diagrams, the initial dilatation of amyl alcohol is 0.001056.

PLATE II

Isothermal Compressibility

.0₂14
.0₂10
.0₂6
.0₂2
0

40°-60°
60°-80°
20°-40°

40°

0 1 2 3 4 5 6 7 8 9 10 11 12
Pressure, kgm. / cm.² x 10⁻³
Methyl Alcohol
Figure 33.

Isothermal Compressibility

.0₂18
.0₂14
.0₂10
.0₂6
.0₂2

40°-60°
20°-40°

40°

0 1 2 3 4 5 6 7 8 9 1
Pressure, kgm. / cm.² x 10⁻³
Ether
Figure 38.

Isothermal Compressibility

.0₂14
.0₂10
.0₂6
.0₂2
0

80°-40°-60°
80°
20°-40°

40°

0 1 2 3 4 5 6 7 8 9 10 11 12
Pressure, kgm. / cm.² x 10⁻³
Ethyl Alcohol
Figure 34.

Isothermal Compressibility

.0₂14
.0₂10
.0₂6
.0₂2
0

60°
80°
40°-60°
20°-40°

40°

0 1 2 3 4 5 6 7 8 9 1
Pressure, kgm. / cm.² x 10⁻³
Acetone
Figure 39.

Compressibility

.0₂14
.0₂10

60°
80°
40°-60°
80°
20°-40°

Compressibility

.0₂14
.0₂10

60°
80°
40°-60°

40°

Figure 42.

Ethyl Chloride

Figure 43.

Ethyl Bromide

Figure 33.

Ether

Figure 38.

.0₂14

.0₂10

Isothermal Compressibility

.0₄6

.0₄2

0

80° 40°
80° 60°

20° 40°

40°

0 1 2 3 4 5 6 7 8 9 10 11 12

Pressure, kgm. / cm.² x 10⁻³

Ethyl Alcohol

Figure 34.

.0₂2

.0₂1

0

.0₂1

.0₂14

.0₂10

Isothermal Compressibility

.0₄6

.0₄2

0

60° 40° 60°
80°
20° 40°

40°

0 1 2 3 4 5 6 7 8 9 10 11 12

Pressure, kgm. / cm.² x 10⁻³

Propyl Alcohol

Figure 35.

.0₂2

.0₂1

0

.0₂1

.0₂14

.0₂10

Isothermal Compressibility

.0₄6

.0₄2

0

60° 80°
40° 60°

20° 40°

40°

0 1 2 3 4 5 6 7 8 9 10 11 12

Pressure, kgm. / cm.² x 10⁻³

Isobutyl Alcohol

Figure 36.

.0₂1

0

.0₂1

.0₂14

.0₂10

Isothermal Compressibility

.0₄6

.0₄2

0

80°
80°

40° 60°

20° 40°

40°

0 1 2 3 4 5 6 7 8 9 10 11

Pressure, kgm. / cm.² x 10⁻³

Acetone

Figure 39.

.0₂14

.0₂10

Isothermal Compressibility

.0₄6

.0₄2

0

60°
80°
40° 60°

20° 40°

40°

0 1 2 3 4 5 6 7 8 9 10 11

Pressure, kgm. / cm.² x 10⁻³

Carbon Bisulphide

Figure 40.

.0₂14

.0₂10

Isothermal Compressibility

.0₄6

.0₄2

0

40° 60°
60° 80°

20° 40°

40°

0 1 2 3 4 5 6 7 8 9 10 11

Pressure, kgm. / cm.² x 10⁻³

Phosphorus Trichloride

Figure 41.

Folder II. Isothermal compressibility, $\left(\frac{\partial v}{\partial p}\right)_T$, against pressu
33 to 44 give the compressibility of the liquids separately at inte
and Figure 45 shows the average between 20° and 80° for all two
In order to avoid confusion in the diagrams the following course
The compressibility at 40° is given over the entire pressure ran
4000 b.a.r, the compressibilities at 20°, 60° and 80° are also shown

Isothermal Compressibility

.0₂14 .0₁1
.0₂10 0
.0₂6 .0₁1
.0₂2 .0₂2
.0₃3

40° 60° 60° 80°
20° 40°
40°

Pressure, kgm. / cm.² x 10⁻³
Ethyl Bromide

FIGURE 43.

Isothermal Compressibility

.0₂14 .0₂2
.0₂10 .0₁1
.0₂6 0
.0₂2 .0₁1
.0₂2

80° 40° 60°
80°
40°
20°
40°

Pressure, kgm. / cm.² x 10⁻³
Ethyl Iodide

FIGURE 44.

Isothermal Compressibility

0.0₂10
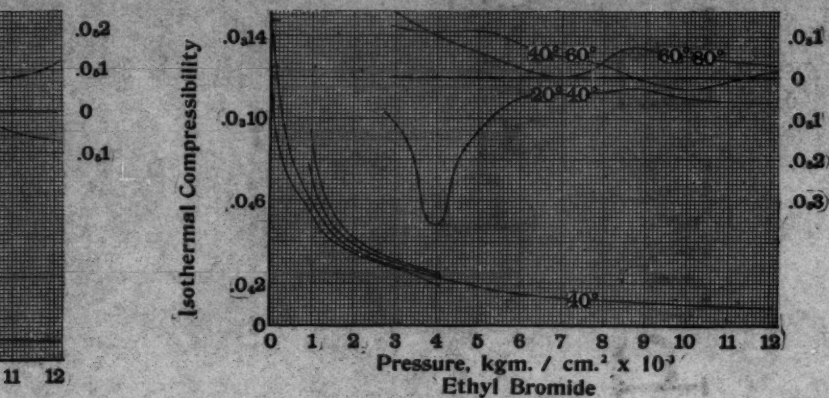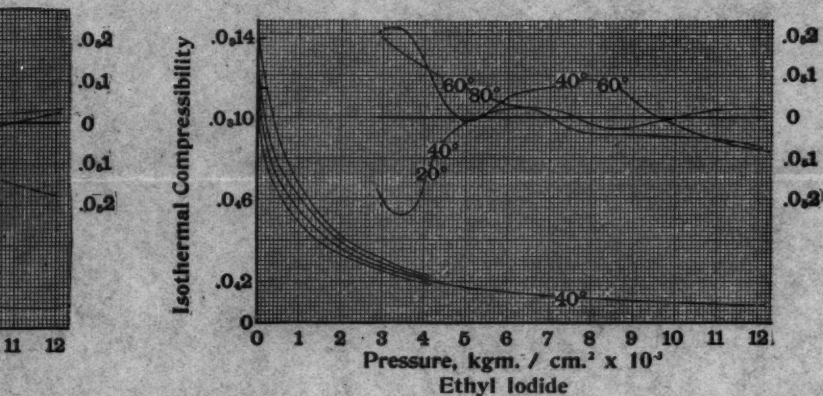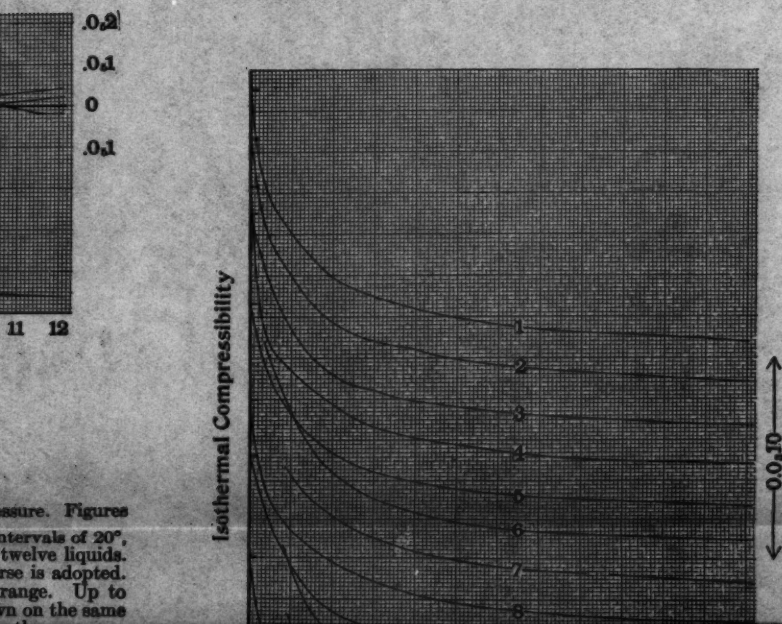
ssure. Figures
ntervals of 20°,
twelve liquids.
rse is adopted.
range. Up to
wn on the same

Isothermal Compressibility

.0.2

0

0 1 2 3 4 5 6 7 8 9 10 11 12

Pressure, kgm. / cm.² x 10⁻³

Propyl Alcohol

FIGURE 35.

Isothermal

.0.2

0

0 1 2 3 4 5 6 7 8 9 10

Pressure, kgm. / cm.² x 10⁻³

Carbon Bisulphide

FIGURE 40.

Isothermal Compressibility

.0.14 60°80°   40°60°   .0.1
       20°40°   0
.0.14   .0.1
.0.10

.0.6

.0.2   40°

0
0 1 2 3 4 5 6 7 8 9 10 11 12

Pressure, kgm. / cm.² x 10⁻³

Isobutyl Alcohol

FIGURE 36.

Isothermal Compressibility

.0.14   40°60°
             60°80°
.0.10   20°40°

.0.6

.0.2   40°

0
0 1 2 3 4 5 6 7 8 9 10

Pressure, kgm. / cm.² x 10⁻³

Phosphorus Trichloride

FIGURE 41.

Isothermal Compressibility

.0.10   40°60°   60°80°   .0.1
                                            0
.0.6   20°40°   .0.1

.0.2   40°

0
0 1 2 3 4 5 6 7 8 9 10 11 12

Pressure, kgm. / cm.² x 10⁻³

Amyl Alcohol

FIGURE 37.

Folder II. Isothermal compressibility, $\left(\dfrac{\partial v}{\partial p}\right)_T$, against pres
33 to 44 give the compressibility for the liquids separately at in
and Figure 45 shows the average between 20° and 80° for all t
In order to avoid confusion in the diagrams the following cour
The compressibility at 40° is given over the entire pressure r
4000 kgm. the compressibilities at 20°, 60° and 80° are also show
scale, but at the higher pressures, where the difference between
sibilities becomes smaller, the difference for intervals of 20° is
upper right hand of the diagram on a larger scale. The scale o
ence curves is shown at the right hand side. A negative ord
curve 20°–40° indicates that the compressibility is less at 20°
The appearance of the difference curves is the same as would
if the curves of the lower part of the diagram were magnified
and the curve for 40° straightened out into the heavy fiduci
order of the curves in the lower left hand part of the diagram is
all liquids, 20°–40°–60°–80°, reading from below up.
Figure 45 shows the average for the twelve liquids. In order t
lapping, the origin of each curve is displaced one square with
next one. The scale of the curves is shown at the right han
origin is so situated that the compressibility for all twelve liqui
0.0.1 and 0 at 12000 kgm. The numbers on the curves indic
in the same order as the curves for the separate liquids (Figures

.0,2

40°

0 1 2 3 4 5 6 7 8 9 10 11 12

Pressure, kgm. / cm.² x 10⁻³

Ethyl Iodide

Figure 44.

.0,2

.0,1

0

.0,1

11 12
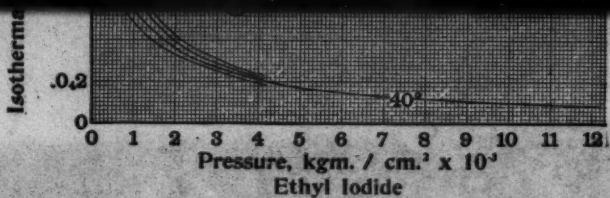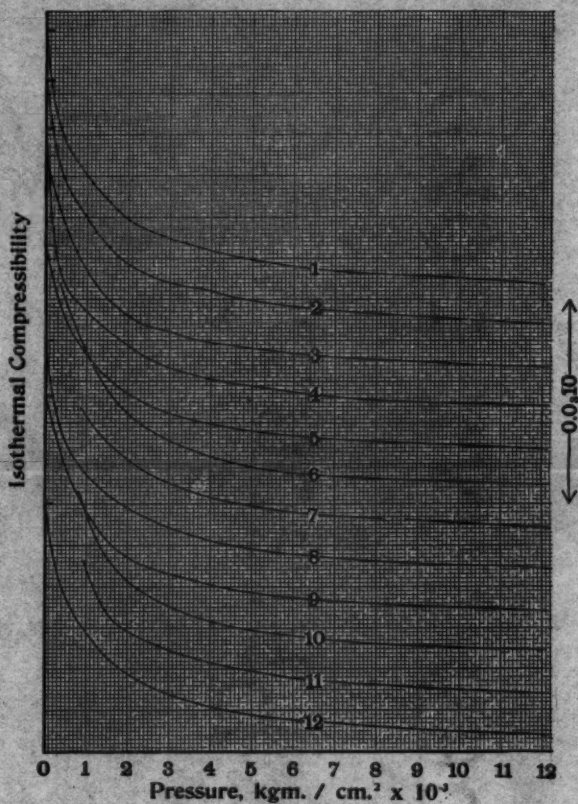
ressure. Figures

intervals of 20°,
l twelve liquids.
urse is adopted.
e range. Up to
wn on the same
en the compres-
is plotted in the
e of these differ-
ordinate for the
20° than at 40°.
ld be presented
d twenty times
ucial line. The
is the same for

er to avoid over-
h respect to the
and side. The
quids is between
licate the liquid
s 33 to 44).

Isothermal Compressibility

0,0,10

1
2
3
4
5
6
7
8
9
10
11
12

0 1 2 3 4 5 6 7 8 9 10 11 12

Pressure, kgm. / cm.² x 10⁻³

Figure 45.

FIGURE 47.

Methyl Alcohol

FIGURE 52.

Ether

Ethyl Alcohol

FIGURE 48.

Pressure, kgm. / cm.² x 10³'
Ethyl Chloride

FIGURE 56.

Work of compression, kgm. m.

40°
60° 80°
40° 60°
20° 40°

0 1 2 3 4 5 6 7 8 9 10 11 12
Pressure, kgm. / cm.² x 10⁻³
Ethyl Alcohol

Figure 48.

Work of compression, kgm. m.

40°
60° 80°
40° 60°

0 1 2 3 4 5 6 7 8 9 10 11 12
Pressure, kgm. / cm.² x 10⁻³
Propyl Alcohol

Figure 49.

Work of compression, kgm. m.

40°
60° 80°
40° 80°
20° 40°

0 1 2 3 4 5 6 7 8 9
Pressure, kgm. / cm.² x 10⁻³
Acetone

Figure 53.

Work of compression, kgm. m.

40°
60° 80°
40° 60°
20° 40°

0 1 2 3 4 5 6 7 8 9
Pressure, kgm. / cm.² x 10⁻³
Carbon Bisulphide

Figure 54.

compression, kgm. m.

40°

m. m.

Work of compression, kgm. m.

10
8
6
4
2
0

40°
60° 80°
40°-60°
20°-40°

0 1 2 3 4 5 6 7 8 9 10 11 12
Pressure, kgm. / cm.² x 10⁻³
Ethyl Bromide

FIGURE 57.

Work of compression, kgm. m.

10
8
6
4
2
0

40°
60° 80°
40°-60°
20°-40°

0 1 2 3 4 5 6 7 8 9 10 11 12
Pressure, kgm. / cm.² x 10⁻³
Ethyl Iodide
FIGURE 58.

Propyl Alcohol

FIGURE 49.

Isobutyl Alcohol

FIGURE 50.

Pressure, kgm. / cm.² x 10⁻³

Carbon Bisulphide

FIGURE 54.

Pressure, kgm. / cm.² x 10⁻³

Phosphorus Trichloride

FIGURE 55.

Amyl Alcohol

FIGURE 51.

Folder III. The work of compression $\left(W = \int p\, dv \right)$ aga

Figures 47 to 58 W is shown for the liquids separately, and
average between 20° and 80° for all twelve liquids. The wo
varies very little with the temperature, so in order to avo
complete curve for only 40° is given, and in addition, in the
diagram, on a scale one hundred times as large, the differen
20° intervals. Each of these difference curves starts from a r
for example, the work of compression of ethyl iodide at 60
is found to be 4.30 (the work of compression at 40°) plus 0.
between the work at 40° and 60°), plus 0.30 (the difference
at 60° and 80°), or 4.83 kgm. m. in all. In Figure 59, gi
work of compression over the entire temperature range, t
cate the liquids in the same order as the immediately pre
the separate liquids. In order to avoid confusion, the orig
is displaced one square with respect to the next one. The b
for acetone (7) is because of the freezing, which made it po
average only from 40° to 80° over the upper part of the pr
stead of between 20° and 80° as at the lower pressures.
curve for ethyl chloride (10) is at 500 kgm. instead of atm
as for the other liquids, because of the low boiling point of
atmospheric pressure.

Work of compression

60° 80°

40° 60°

20° 40°

0 1 2 3 4 5 6 7 8 9 10 11 12

Pressure, kgm. / cm.² x 10⁻³

Ethyl Iodide
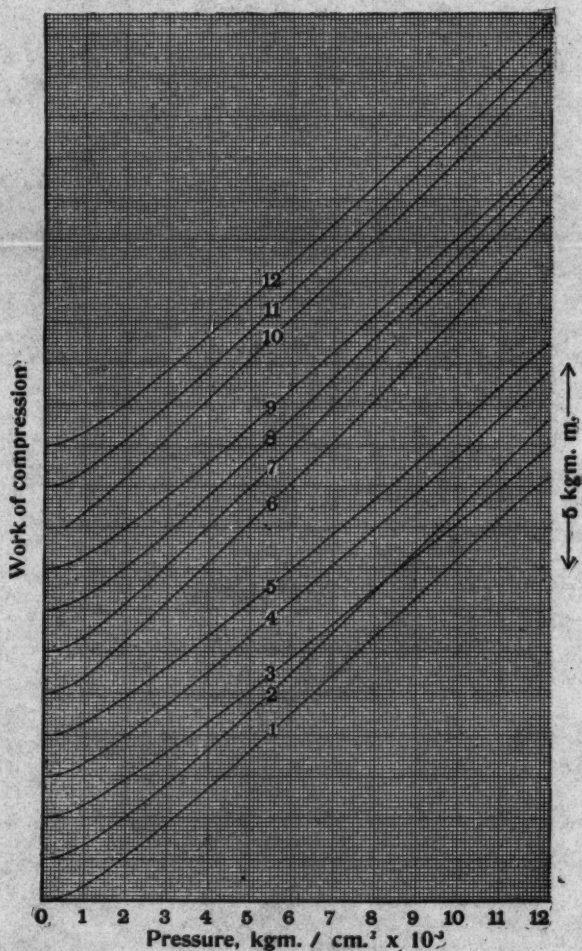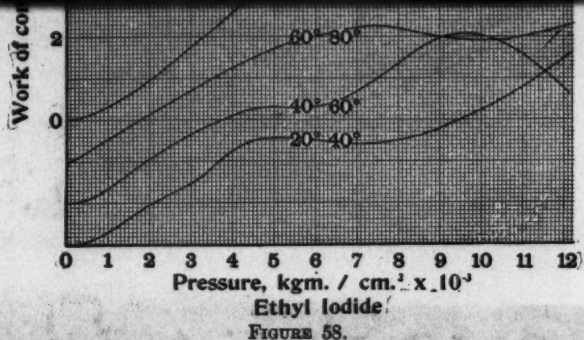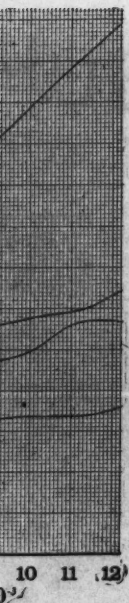
FIGURE 58.

against pressure. In
and in Figure 59 the
work of compression
avoid confusion, the
the lower part of the
erence of the work at
a new origin. Thus
t 6000 kgm. and 80°
s 0.23 (the difference
ce between the work
, giving the average
e, the numbers indi-
preceding figures for
origin of each curve
he break in the curve
t possible to take the
e pressure range, in-
. The origin of the
atmospheric pressure
t of this substance at

Work of compression

12
11
10

9
8
7

6

5
4

3
2

1

5 kgm. m.

0 1 2 3 4 5 6 7 8 9 10 11 12

Pressure, kgm. / cm.² x 10⁻³

FIGURE 59.

FOLDER IV.

Heat of compression

in kg/m

Methyl Alcohol

Pressure p. kg/cm² x 10³

Heat of compression

Heat of compression

← 10 kgm. m. →

0 1 2 3 4 5 6 7 8 9 10 11 12

Pressure, kgm. / cm.² x 10⁻³

Methyl Alcohol

FIGURE 60.

Heat of compression

0 1 2 3 4 5 6 7 8 9 10 11 12

Pressure, kgm. / cm.² x 10⁻³

Ether

FIGURE 65.

Heat of compression

← 10 kgm. m. →

0 1 2 3 4 5 6 7 8 9 10 11 12

Pressure, kgm. / cm.² x 10⁻³

Ethyl Alcohol

FIGURE 61.

Heat of compression

0 1 2 3 4 5 6 7 8 9 10 11

Pressure, kgm. / cm.² x 10⁻³

Acetone

FIGURE 66.

Ethyl Chloride

FIGURE 69.

Ethyl Iodide

FIGURE 70.

FIGURE 60.

Heat of compression

80°
60°
40°
20°

← 10 kgm. m. →

0 1 2 3 4 5 6 7 8 9 10 11 12
Pressure, kgm. / cm.² x 10⁻³
Ethyl Alcohol

FIGURE 61.

Heat of compression

80°
60°
40°
20°

← 10 kgm. m. →

0 1 2 3 4 5 6 7 8 9 10 11 12
Pressure, kgm. / cm.² x 10⁻³
Propyl Alcohol

FIGURE 62.

FIGURE 66.

Heat of compression

80°
60°
40°
20°

← 10 kgm. m. →

0 1 2 3 4 5 6 7 8 9 10 11 12
Pressure, kgm. / cm.² x 10⁻³
Acetone

FIGURE 67.

Heat of compression

80°
60°
40°
20°

← 10 kgm. m. →

0 1 2 3 4 5 6 7 8 9 10 11 12
Pressure, kgm. / cm.² x 10⁻³
Carbon Bisulphide

Heat of compression

80°
60°
40°
20°

10 kgm. m.

0 1 2 3 4 5 6 7 8 9 10 11 12

Pressure, kgm. / cm.² x 10⁻³

Ethyl Iodide

FIGURE 70.

Heat of compression

10 kgm. m.

80°
60°
40°
20°

10 kgm. m.

0 1 2 3 4 5 6 7 8 9 10 11 12

Pressure, kgm. / cm.² x 10⁻³

Ethyl Bromide

FIGURE 71.

Pressure, kgm. / cm.² x 10⁻³
Propyl Alcohol

FIGURE 62.

Pressure, kgm. / cm.² x 10⁻³
Isobutyl Alcohol

FIGURE 63.

Pressure, kgm. / cm.² x 10⁻³
Carbon Bisulphide

FIGURE 67.

Pressure, kgm. / cm.² x 10⁻³
Phosphorus Trichloride

FIGURE 68.

Pressure, kgm. / cm.² x 10⁻³
Amyl Alcohol
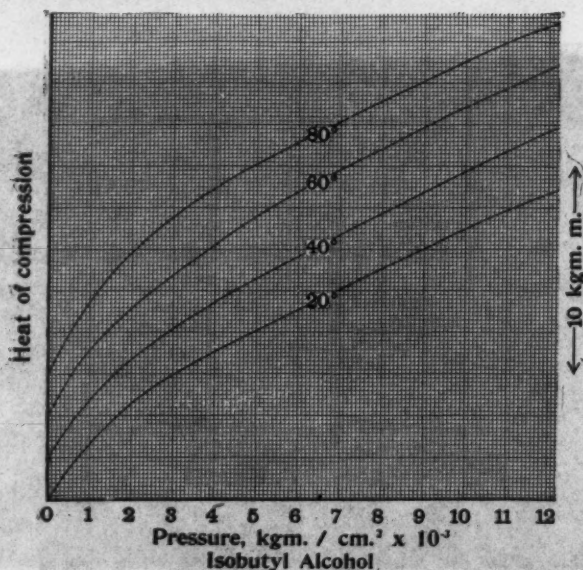
FIGURE 64.

Folder IV. The heat of compression $\left(Q = f_\tau \left(\frac{\partial v}{\partial \tau}\right), dv\right)$ against pressure. In Figures 60 to 71 are shown the curves for the separate liquids intervals of temperature of 20°. In order to avoid overlapping, the origin different temperatures is not the same. The scale of the diagram is shown the right hand side. Because of the low boiling point, some of the curves not start from an origin at atmospheric pressure. Figure 72 shows the average heat of compression between 20° and 80° for all twelve liquids. The origin each curve is displaced one square with respect to the next. Ethyl chlor (10) and ether (6) start from an origin at 500 kgm. because of the low boil point. The curve for acetone (7) shows a break at 8000 kgm. because ab 8000 the average had to be taken between 40° and 80° by reason of the free ing under pressure. The numbers in Figure 72 indicate the liquids in same order as that of the separate diagrams.

Pressure, kgm. / cm.² x 10⁻³
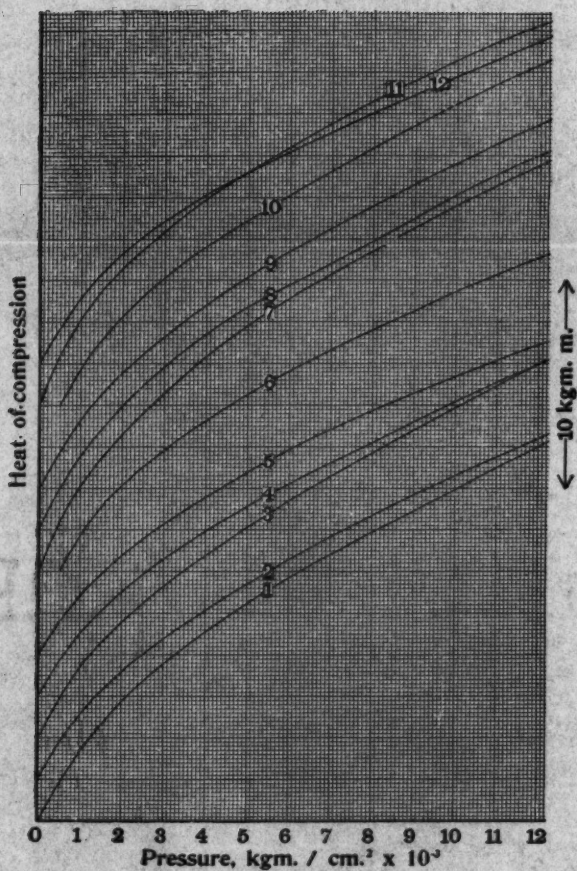
Ethyl Bromide

Figure 71.

Heat of compression

10 kgm. m.

Pressure, kgm. / cm.² x 10⁻³

Figure 72.
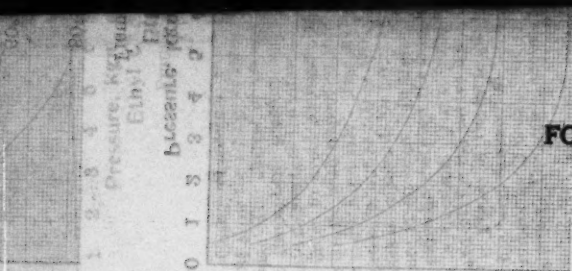
pres-
ids at
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wn at
ves do
verage
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loride
oiling
above
freez-
n the

FOLDER V.

Change of Internal Energy

Pressure kg/cm² × 10²

Change of Internal Energy

Change of Internal Energy vs Pressure, kgm. / cm.² x 10⁻³

Methyl Alcohol

Figure 73.

Change of Internal Energy vs Pressure, kgm. / cm.² x 10⁻³

Ethyl Alcohol

Figure 74.

Change of Internal Energy vs Pressure, kgm. / cm.² x 10⁻³

Ether

Figure 78.

Change of Internal Energy vs Pressure, kgm. / cm.² x 10⁻³

Acetone

Figure 79.

Change of Internal Energy,

5 kgm. m.

80°
60°
40°
20°

0 1 2 3 4 5 6 7 8 9 10 11 12
Pressure, kgm. / cm.² x 10⁻³
Ethyl Bromide,
FIGURE 83.

Change of Internal Energy,

5 kgm. m.

60°
40° 80°
20°

0 1 2 3 4 5 6 7 8 9 10 11 12
Pressure, kgm. / cm.² x 10⁻³
Ethyl Iodide
FIGURE 84.

Change of Internal Energy

80°

60°

40°

20°

5 kgm. m.

0 1 2 3 4 5 6 7 8 9 10 11 12
Pressure, kgm. / cm.² x 10⁻³
Ethyl Alcohol

FIGURE 74.

Change of Internal Energy

80°

60°

40°

20°

5 kgm. m.

0 1 2 3 4 5 6 7 8 9 10 11 12
Pressure, kgm. / cm.² x 10⁻³
Propyl Alcohol

FIGURE 75.

Change of Internal Energy

60°

40°

20°

0 1 2 3 4 5 6 7 8 9 10 11
Pressure, kgm. / cm.² x 10⁻³
Acetone

FIGURE 79.

Change of Internal Energy

80°

60°

40°

20°
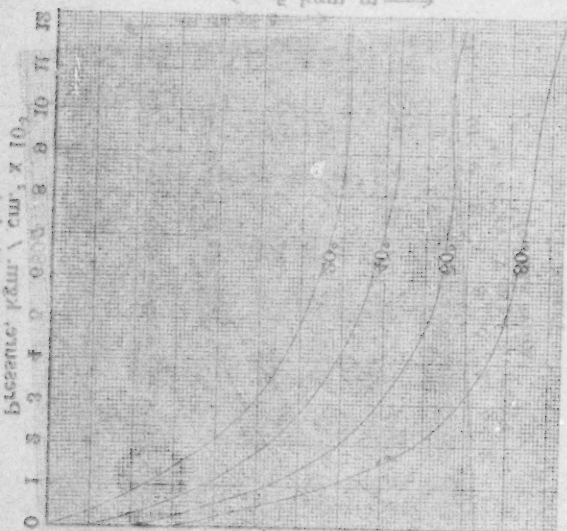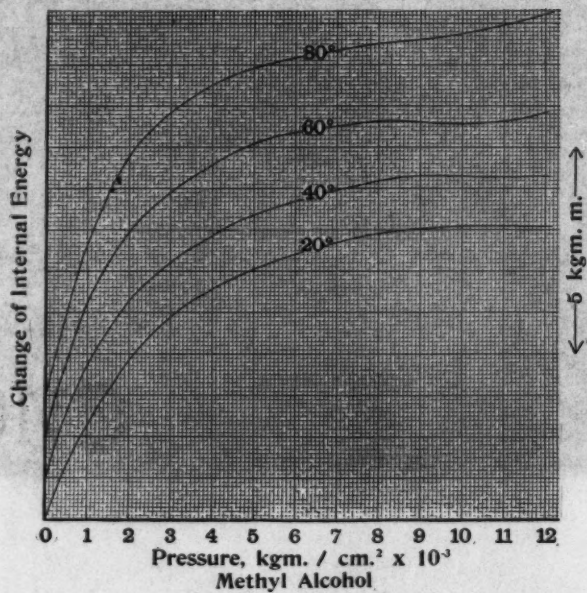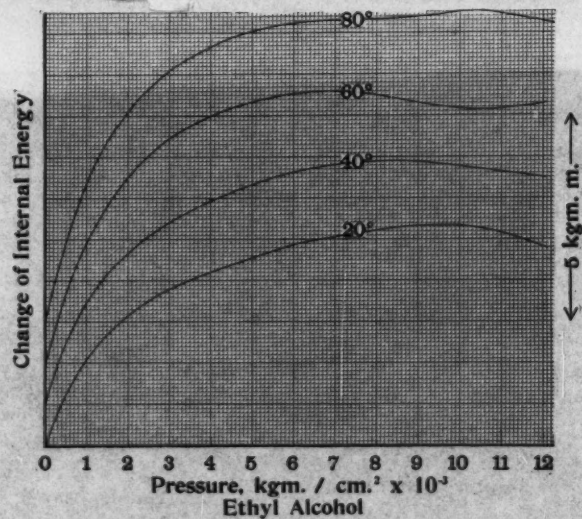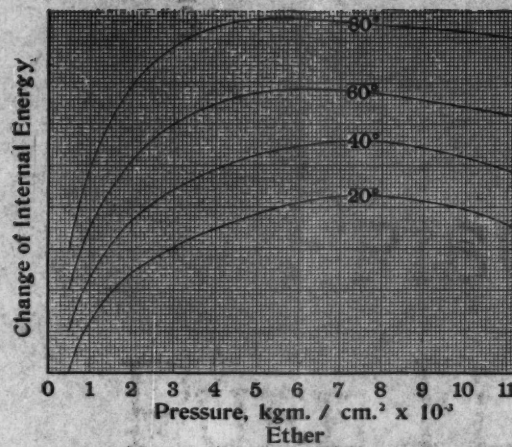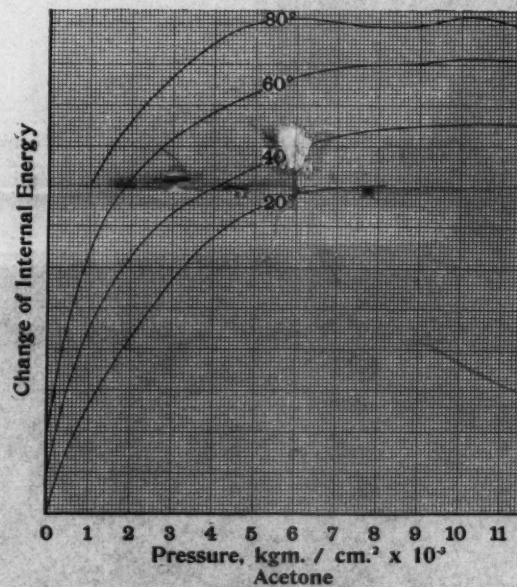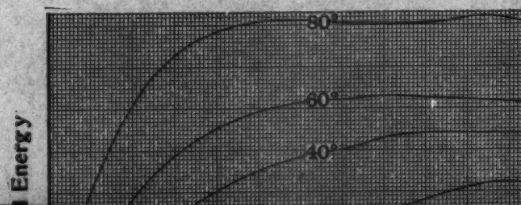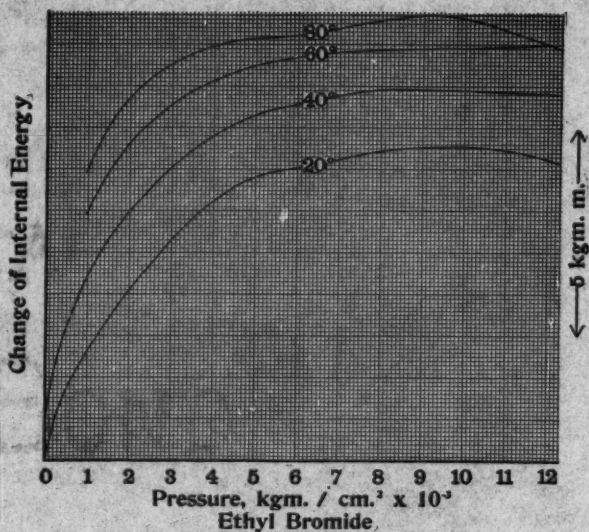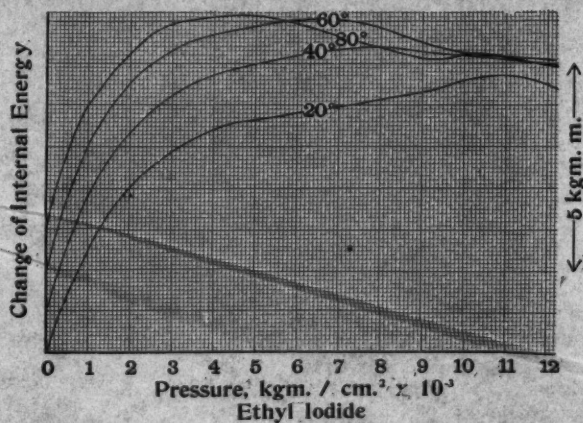
0 1 2 3 4 5 6 7 8 9 10 11
Pressure, kgm. / cm.² x 10⁻³
Carbon Bisulphide

FIGURE 80.

Change of Internal Energy

80°

60°

40°

20°

Ethyl Bromide

FIGURE 83.

Change of Internal Energy (vertical axis)

5 kgm. m. (left and right margins)

60°
80°
40°
20°

Pressure, kgm. / cm.² x 10⁻³

Ethyl Iodide

FIGURE 84.

Change of Internal Energy (vertical axis)

5 kgm. m. (left and right margins)

11
12
10
9
8
7
6
5
3
4
2
1

Pressure, kgm. / cm.² x 10⁻³

Pressure, kgm. / cm.² x 10⁻³

Propyl Alcohol

FIGURE 75.

Change of Internal Energy

5 kgm. m.

Pressure, kgm. / cm.² x 10⁻³

Isobutyl Alcohol

FIGURE 76.

Change of Internal Energy

5 kgm. m.

Pressure, kgm. / cm.² x 10⁻³

Amyl Alcohol

FIGURE 77.

Change of Internal Energy

Pressure, kgm. / cm.² x 10⁻³

Phosphorus Trichloride

FIGURE 81.

Change of Internal Energy

Pressure, kgm. / cm.² x 10⁻³

Ethyl Chloride

FIGURE 82.

Folder V. Change of internal energy, $\Delta E = Q - W$, against p
Figures 73 to 84 show the change of internal energy at intervals of 20
separate liquids. The change of energy plotted is the difference
the energy at atmospheric pressure and the pressure in question, so
positive ordinate means that the internal energy has decreased with in
pressure. In order to avoid confusion, the origin of the separate c
displaced one square with respect to the next. The scale of the dia
shown at the right hand side. The origin of some of the curves is
atmospheric pressure, but at 500 or 1000 kgm. This is because the b
ing point makes it impossible to carry the liquid to atmospheric pre
the temperature in question. In these cases, the change of internal
shown is the difference between the internal energy at 500 or 1000 k
the pressure in question. Figure 85 shows the average change of
between 20° and 80° for the twelve liquids plotted in a single diagram
pressure, and in Figure 86, the same quantity against volume. The o
these curves has been displaced in the usual way, and the liquids ha
shown by numbers as is usual, (the order being the same as that
separate diagrams.) The scale is shown at the right hand side.
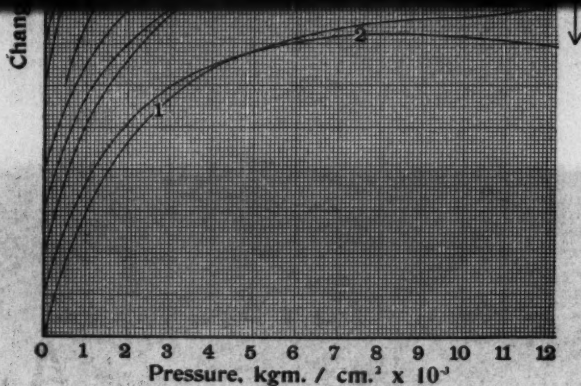
FIGURE 85.
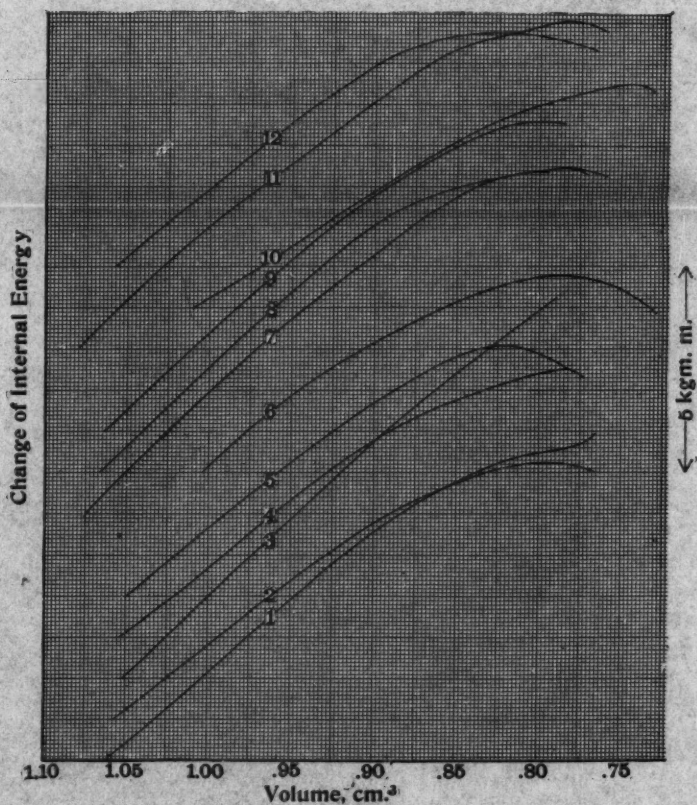
FIGURE 86.

t pressure.
20° for the
ce between
, so that a
increasing
e curves is
diagram is
s is not at
e low boil-
pressure at
nal energy
kgm. and
of energy
am against
e origin of
have been
hat of the

Change of C_p

Pressure, kgm. / cm.² x 10⁻³
Methyl Alcohol

FIGURE 87.

Change of C_p

Pressure, kgm. / cm.² x 10⁻³
Ethyl Alcohol

FIGURE 88.

Change of C_p

Pressure, kgm. / cm.² x 10⁻³
Amyl Alcohol

FIGURE 91.

Change of C_p

Change of C_p

10 kgm. cm.

80°
40°
80°
20°

0 1 2 3 4 5 6 7 8 9 10 11 12
Pressure, kgm. / cm.^{2} x 10^{-3}
Phosphorus Trichloride

FIGURE 95.

Change of C_p

10 kgm. cm.

40°
60°
90°

80°

0 1 2 3 4 5 6 7 8 9 10 11 12
Pressure, kgm. / cm.^{2} x 10^{-3}
Ethyl Chloride

FIGURE 96.

Change of C_p

10 kgm. cm.

80°
60°
40°
20°

0 1 2 3 4 5 6 7 8 9 10 11 12
Pressure, kgm. / cm.^{2} x 10^{-3}

Pressure, kgm. / cm.² x 10⁻³
Methyl Alcohol

Figure 87.

Change of C_p

← 10 kgm. cm. →

80°
60°
40°
20°

0 1 2 3 4 5 6 7 8 9 10 11 12
Pressure, kgm. / cm.² x 10⁻³
Ethyl Alcohol

Figure 88.

Change of C_p

← 10 kgm. cm. →

80°
60°
40°
20°

0 1 2 3 4 5 6 7 8 9 10 11 12
Pressure, kgm. / cm.² x 10⁻³
Propyl Alcohol

Figure 89.

Change of C_p

60°
40°
80°

Change of C_p

80°

40°

20°

0 1 2 3 4 5 6 7 8 9 10 11 12
Pressure, kgm. / cm.² x 10⁻³
Amyl Alcohol

Figure 91.

Change of C_p

← 10 kgm. cm. →

80°
60°
40°
20°

0 1 2 3 4 5 6 7 8 9 10 11 12
Pressure, kgm. / cm.² x 10⁻³
Ether

Figure 92.

Change of C_p

← 10 kgm. cm. →

80°
60°
40°
60° 80°
40°

20°

0 1 2 3 4 5 6 7 8 9 10 11 12
Pressure, kgm. / cm.² x 10⁻³
Acetone

Figure 93.

Change of C_p

0   1   2   3   4   5   6   7   8   9   10 11 12
Pressure, kgm. / cm.² x 10⁻³
Ethyl Chloride

FIGURE 96.

Change of C_p

80°
60°
40°
20°

0   1   2   3   4   5   6   7   8   9   10 11 12
Pressure, kgm. / cm.² x 10⁻³
Ethyl Bromide

FIGURE 97.

Change of C_p

60° 40° 20°

80°

0   1   2   3   4   5   6   7   8   9   10 11 12
Pressure, kgm. / cm.² x 10⁻³
Ethyl Iodide

FIGURE 98.

Pressure, kgm. / cm.² x 10⁻³

Propyl Alcohol

FIGURE 89.

Pressure, kgm. / cm.² x 10⁻³

Isobutyl Alcohol

FIGURE 90.

Ether

FIGURE 92.

Pressure, kgm. / cm.² x 10⁻³

Acetone

FIGURE 93.

Pressure, kgm. / cm.² x 10⁻³

Carbon Bisulphide

FIGURE 94.

Folder VI. The change of specific heat at constant pressure (C_p) against pressure. Note that the units in which C_p are measured are the number of kgm. cm. of work necessary to raise through one degree the quantity of liquid which at 0° C. and atmospheric pressure occupies one c.c. Figures 87 to 98 show the change of C_p at intervals of 20° for the liquids separately. A positive ordinate means that C_p is greater at atmospheric pressure than at the pressure in question. The origin of each of the curves has been displaced with respect to the next in the usual way, and the scale is shown at the right hand side. Because of the low boiling point, the origin for some of the curves is at 500 or 1000 kgm. In these cases, the difference shown is the difference between C_p at 500 or 1000 kgm. and the pressure in question. Figure 99 shows the average of C_p from 20° to 80° for all twelve liquids. The liquids are indicated by numbers, the origin of the separate curves has been displaced, and the scale is shown at the right hand side, in the usual way.

Change of C_p

Pressure, kgm. / cm.^{2} x 10^{-3}

Ethyl Iodide

FIGURE 98.

Change of C_p

Pressure, kgm. / cm.^{2} x 10^{-3}
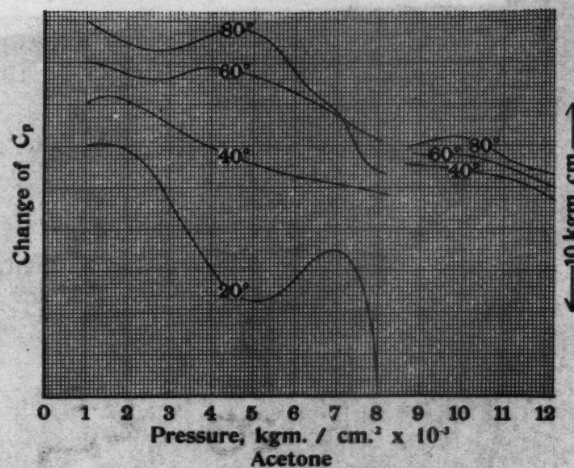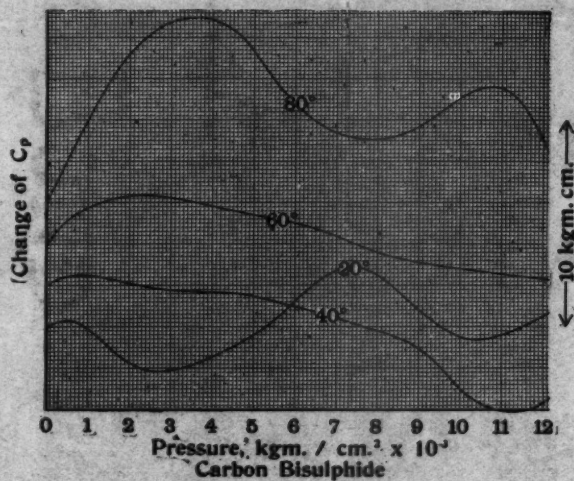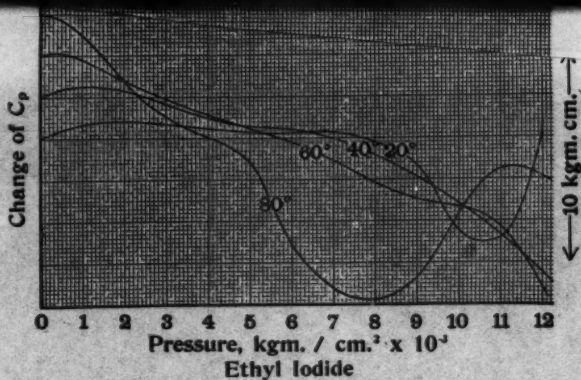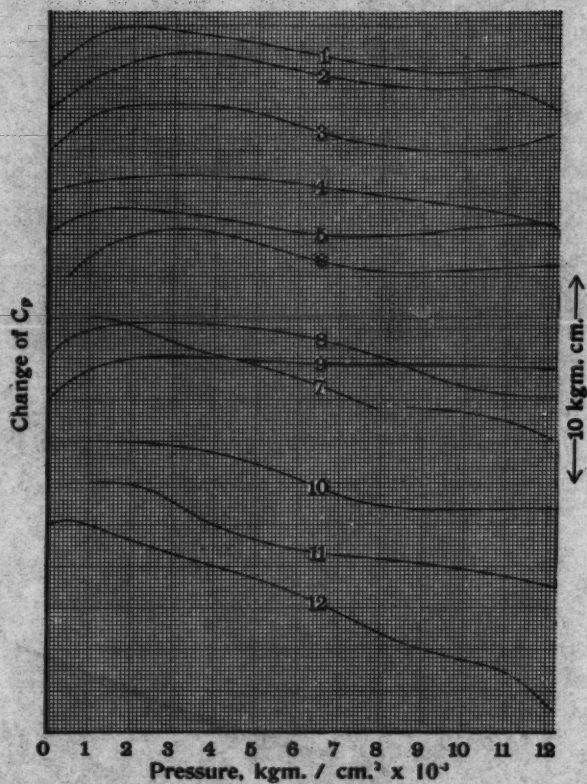
FIGURE 99.

Isobutyl Alcohol

Pressure, kgm. / cm.² × 10⁴

Figure 102.

Change of C_v

80°
60°
40°
20°

0 1 2 3 4 5 6 7 8 9 10 11 12
Pressure, kgm. / cm.² x 10⁻³
Methyl Alcohol

10 kgm. cm.

FIGURE 100.

Change of C_v

80°

40°

20°

0 1 2 3 4 5 6 7 8 9 10 11 12
Pressure, kgm. / cm.² x 10⁻³
Amyl Alcohol

10 kgm. cm.

FIGURE 104.

Change of C_v

80°
60°
40°
20°

0 1 2 3 4 5 6 7 8 9 10 11 12
Pressure, kgm. / cm.² x 10⁻³
Ethyl Alcohol

10 kgm. cm.

FIGURE 101.

Change of C_v

80°
60°
40°
20°

0 1 2 3 4 5 6 7 8 9 10 11 12
Pressure, kgm. / cm.² x 10⁻³
Ether

10 kgm. cm.

Phosphorus Trichloride

FIGURE 108.

Ethyl Chloride

FIGURE 109.

Pressure, kgm. / cm.² x 10⁻³
Methyl Alcohol

Figure 100.

Change of C_v

80°
60°
40°
20°

10 kgm. cm.

2

0 1 2 3 4 5 6 7 8 9 10 11 12

Pressure, kgm. / cm.² x 10⁻³
Ethyl Alcohol

Figure 101.

40°
20°

0 1 2 3 4 5 6 7 8 9 10 11 12

Pressure, kgm. / cm.² x 10⁻³
Amyl Alcohol

Figure 104.

Change of C_v

80°
60°
40°
20°

10 kgm. cm.

0 1 2 3 4 5 6 7 8 9 10 11 12

Pressure, kgm. / cm.² x 10⁻³
Ether

Figure 105.

Change of C_v

80°
60°
40°
20°

10 kgm. cm.

0 1 2 3 4 5 6 7 8 9 10 11 12

Pressure, kgm. / cm.² x 10⁻³
Propyl Alcohol

Figure 102.

Change of C_v

80°
60°
40°
20°

80°
40° 60°

10 kgm. cm.

0 1 2 3 4 5 6 7 8 9 10 11 12

Pressure, kgm. / cm.² x 10⁻³
Acetone

Figure 106.

80°

of C_v

cm.

Change of C_v

40°
20°
80°

10 kgm. cm.

Pressure, kgm. / cm.² x 10⁻³
Ethyl Chloride

FIGURE 109.

Change of C_v

80°
60°
40°
20°

10 kgm. cm.

Pressure, kgm. / cm.² x 10⁻³
Ethyl Bromide

FIGURE 110.

Change of C_v

20°
40°
60°
80°

10 kgm. cm.

Pressure, kgm. / cm.² x 10⁻³
Ethyl Iodide

FIGURE 111.

Change of C_v

10 kgm. cm.

80°
60°
40°
20°

0 1 2 3 4 5 6 7 8 9 10 11 12

Pressure, kgm. / cm.² x 10⁻³

Propyl Alcohol

FIGURE 102.

Change of C_v

10 kgm. cm.

60°
40°
80°
20°

0 1 2 3 4 5 6 7 8 9 10 11 12

Pressure, kgm. / cm.² x 10⁻³

Isobutyl Alcohol

FIGURE 103.

Change of C_v

10 kgm. cm.

80°
40°
20°

80°
40° 60°

0 1 2 3 4 5 6 7 8 9 10 11 12

Pressure, kgm. / cm.² x 10⁻³

Acetone

FIGURE 106.

Change of C_v

10 kgm. cm.

80°
20°
60°
40°

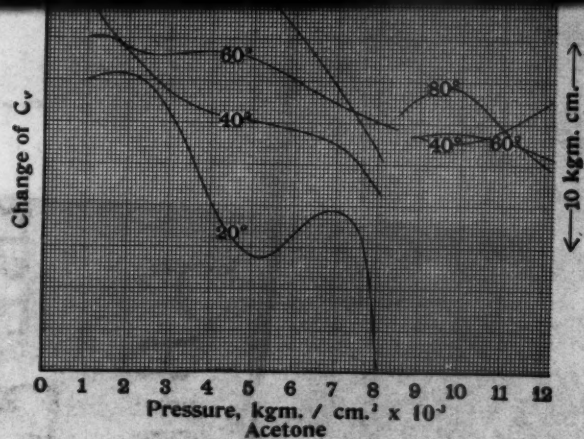0 1 2 3 4 5 6 7 8 9 10 11 12
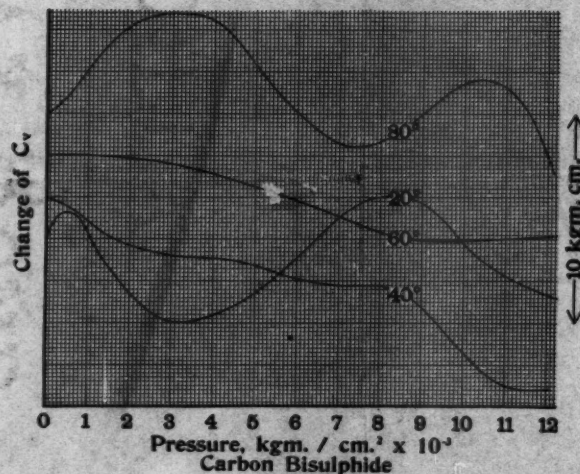
Pressure, kgm. / cm.² x 10⁻³

Carbon Bisulphide

FIGURE 107.

Folder VII. The change of specific heat at constant volume (C_v) against pressure. Note that the units in which C_v is measured are the number of kgm. cm. of work necessary to raise through one degree the quantity of liquid which at 0° C. and atmospheric pressure occupies one c.c. Figures 100 to 111 show the change of C_v for intervals of 20° for the liquids separately. A positive ordinate means that C_v is greater at atmospheric pressure than at the pressure in question. The origin of each curve has been displaced with respect to the next in the usual way, and the scale is shown at the right hand side. Because of the low boiling point, the origin of some of the curves is at 500 or 1000 kgm. In these cases, the difference shown is the difference between C_v at 500 or 1000 kgm. and the pressure in question. Figure 112 shows the average of C_p from 20° to 80° for all twelve liquids. The liquids are indicated by numbers, the origin of the separate curves has been displaced, and the scale is shown at the right hand side, in the usual way.
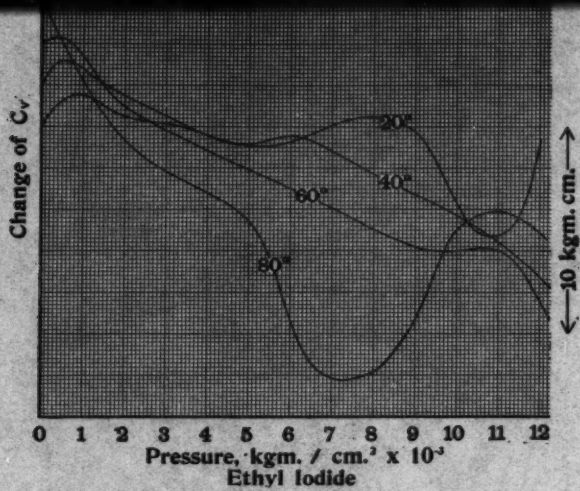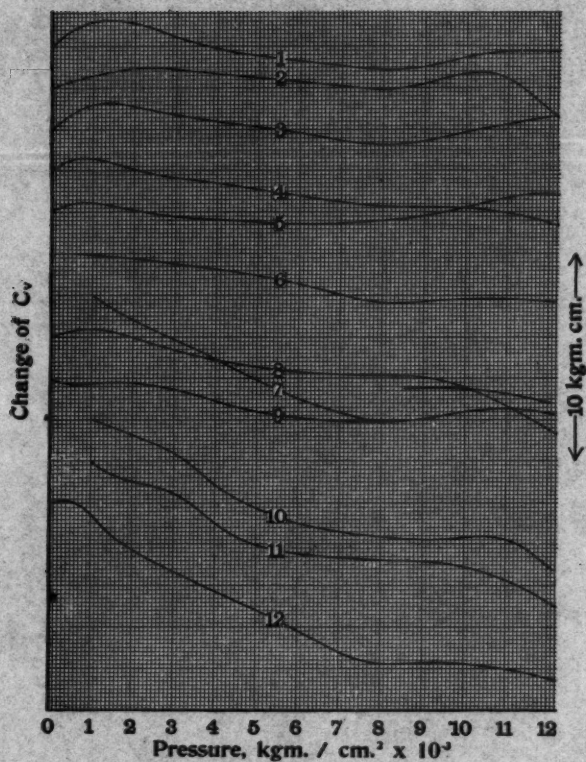
Change of C_v

0 1 2 3 4 5 6 7 8 9 10 11 12
Pressure, kgm. / cm.² x 10⁻³
Ethyl Iodide

Figure 111.

Change of C_v

0 1 2 3 4 5 6 7 8 9 10 11 12
Pressure, kgm. / cm.² x 10⁻³

Figure 112.